

ANALYTICAL ABSTRACTS

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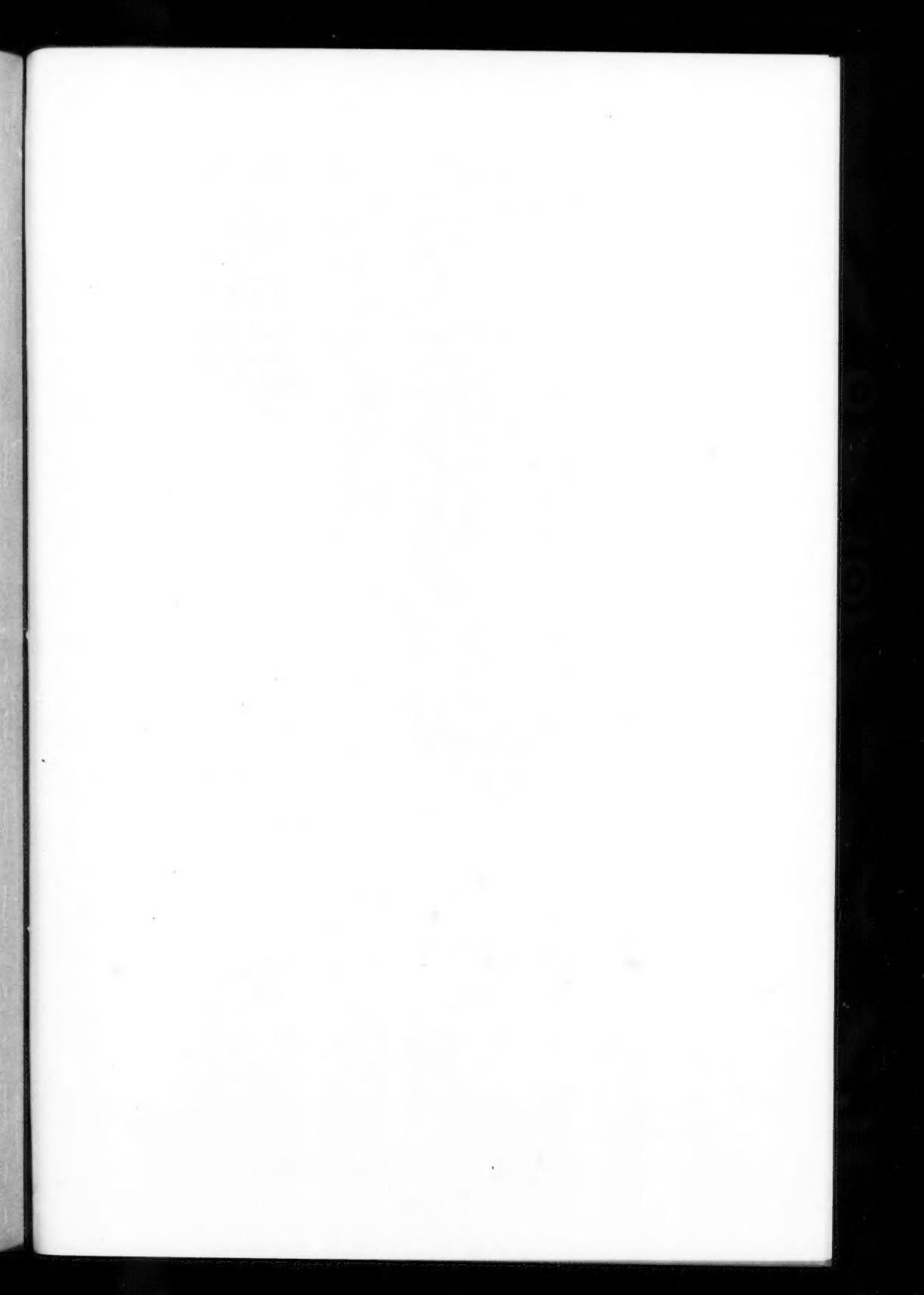
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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1096. Systematic and accidental errors of chemical analysis. V. V. Nalimov. *Zhur. Anal. Khim.*, 1956, **11** (3), 341–350.—Applications of statistics that are of special interest in chemical analysis are considered.

G. S. SMITH

1097. Conscious and unconscious errors in weighing and their influence on the accuracy of micro-analysis. H. Gysel (Pharm. Abteilung CIBA A.-G., Basel). *Mikrochim. Acta*, 1956, (4–6), 577–590.—Individual unconscious errors in the estimation of numbers on balance scales have been investigated. The method suggested in an earlier paper (*Anal. Abstr.*, 1954, **1**, 430) for estimations with improved balance scales have been proven to be of value. The psychological limits of error of up to $\pm 4 \mu\text{g}$ per weighing, published earlier, have been confirmed.

M. F. C. LADD

1098. Required cooling period for porcelain crucibles in desiccators. J. Agterdenbos (Univ. of Amsterdam, Netherlands). *Anal. Chim. Acta*, 1956, **15** (5), 429–434.—Weighing errors that result from incomplete cooling of crucibles have been determined. Each degree difference between crucible temp. and balance temp. can cause errors up to 0·16 mg for the type of crucible used (wt., 13 to 18 g; diam., 45 mm). Errors up to 0·8 mg may be obtained after cooling in a desiccator for 20 to 66 min., according to the number of crucibles in the desiccator. Similarly, cooling periods of 50 to 96 min. result in a 0·3-mg error and periods of 73 to 119 min. result in a 0·16-mg error.

W. C. JOHNSON

1099. The influence of the methyl group on the properties of organic solvents. L. M. Kul'berg, T. I. Badeeva and I. S. Mustafin. *Ukr. Khim. Zhur.*, 1955, **21** (5), 641–645; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,264.—The influence of the position of the CH_3- group in aromatic reagents used analytically is studied. It is established that, in the *para*-position relative to the analytically active groups, the CH_3- group does not influence the properties of the reagent; in the *ortho*-position relative to the $(\text{CH}_3)_2\text{N}-$ group it lowers the sensitivity of the analytical reaction; in the Egrave reaction the use of dimethylaniline increases the sensitivity 4·5 times with respect to dimethyl-*o*-toluidine; in the detection of oxidants, tetramethylbenzidine is several times more sensitive than tetramethyl-*o*-toluidine; the use of crystal violet for the detection of Zn, Cd and Sb by Kuznetsov's method increases the sensitivity 8, 10 and > 40 times, respectively, as compared with the use of its trimethyl analogue. The CH_3- group in the *ortho*-position with respect to other groups may increase the sensitivity of the reagent; in the detection of Fe, 2-hydroxy-*m*-toluic

acid is more sensitive than salicylic acid; in the detection and determination of Cl, *o*-cresol is more sensitive than phenol; *o*-tolylanthranilic acid is a more sensitive reagent for oxidants than phenylanthranilic acid; alumocresone (trimethylaurintricarboxylic acid) gives aluminium and iron lakes with considerably greater mol. coeff. of extinction than aluminon.

C. D. KOPKIN

1100. Studies in analytical chemistry on filter-paper. **XIV. Separation of anions of groups 2 and 3 by paper chromatography.** Shoichi Nakano (Shizuoka Women's College, Shizuoka). *J. Chem. Soc., Japan, Pure Chem. Sect.*, 1956, **77** (5), 673–678.—Chromatographic separation of anions of group 2 (oxalate, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, HF_2^-) and 3 (PO_4^{3-} , AsO_4^{3-} , AsO_3^{3-} , BO_2^- , CO_3^{2-} , SiO_3^{2-} and tartrate) was studied with various developers including those that contain methanol, butanol or acetic acid. The R_F values are summarised under various conditions of pH, concn. of acid, and time of development. The cationic components are removed by passing the soln. through a column of Amberlite IR-120 (H). For the separation of anions of group 2, a mixture of acetic acid and water or benzene is the best, whereas for anions of group 3, methanol containing various electrolytes such as ammonium acetate, aq. NH_3 soln. or Na acetate is suitable.

XV. Separation of the anions of groups 2 and 3 by paper electrophoresis. Shoichi Nakano and Sadako Shimada. *Ibid.*, 1956, **77** (5), 678–682.—A similar experiment was carried out with a simple apparatus for electrophoresis. For the separation of SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_4^{2-}$ and S^{2-} , use of 8 N aq. NH_3 soln. is the best. For anions of group 3, use of M formic acid is recommended.

XVII. Separation of anions of group 4 by paper chromatography. Shoichi Nakano and Sadako Shimada. *Ibid.*, 1956, **77** (6), 833–836.—Chromatographic separation of anions of group 4 [Cl^- , Br^- , I^- , SCN^- , $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$] was studied with developing agents consisting mainly of aliphatic alcohols. "Multiple development" (Jeanes *et al.*, *Anal. Chem.*, 1951, **23**, 415) was found to be especially useful for this purpose; the developed paper is air-dried, and again developed with the same developer in the same direction. A mixture of butanol, conc. aq. NH_3 soln. and collidine (3 + 1 + 1) is the best developer, since the effect of counter ions is minimised.

XVIII. Simultaneous separation of the alkali and alkaline-earth elements by paper chromatography. Shoichi Nakano. *Ibid.*, 1956, **77** (6), 836–839.—When an aq. soln. containing Li^+ , Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} is submitted to paper chromatography with a mixture of acetic acid, ether and HNO_3 (4 + 5 + 1), spots of alkali-earth ions have R_F values $\approx 0\cdot6$, whilst those of alkaline-earth ions have values of 0·1 to 0·3. The separation of each ion can be effected by use of a mixture of methanol, HNO_3 and HCl (8 + 1 + 1). When the

mixture is successively developed along rectangular axes with these two developers, each spot is satisfactorily separated within 10 hr. K. SAITO

1101. Use of some organic compounds as reducing agents. V. Simon and J. Zýka. *Chem. Listy*, 1956, **50** (3), 360-363.—This paper has been published in German in *Coll. Czech. Chem. Commun.*, 1956, **21**, 571 (cf. *Anal. Abstr.*, 1957, **4**, 2). J. ZÝKA

1102. The qualitative reactions of 4-hydroxy-3-mercaptopentolene. V. M. Dzjomko and A. I. Cherepkhanin. *Sbornik Statej Vses. Zaoch. Politekhn. Inst.*, 1955, **11**, 37-43; *Ref. Zhur. Khim.*, 1956, Abstr. No. 32,720.—The qualitative reactions of 4-hydroxy-3-mercaptopentolene (**I**) with inorganic ions are studied, particularly in the presence of pyridine or 1:10-phenanthroline. In a medium 6*N* in HCl, **I** forms coloured products with the following ions, extractable with a mixture of CHCl₃ and isobutyl alcohol—Mo⁶⁺ pink-brown, Re⁷⁺ yellow changing to dark brown, Se⁴⁺ pale yellow, Te⁴⁺ yellow, Pt⁴⁺ pale yellow and V⁸⁺ an unstable blue. Conc. HCl destroys the coloured molybdenum complex, but does not destroy the colour due to Re; this may be used to detect Re in the presence of Mo at a dilution of 1 in 2×10^6 . C. D. KOPKIN

1103. Use of chromatography in qualitative analysis. Stolko Yankov. *Zhur. Anal. Khim.*, 1956, **11** (3), 355.—To detect traces of Mn in the presence of Cr, the solution (0.05 ml) containing 0.6% of HCl is introduced into a micro-column of Al₂O₃ containing 10% of a mixture of KBr and KBrO₃ (1 + 1). With ≤ 0.0035 mg of Mn, a brown colour appears after a few minutes in the middle of the yellow band. By heating with a 60-W lamp, a brown colour can be seen with 0.0017 mg of Mn. To detect Co³⁺ in the presence of Fe²⁺, Fe³⁺, Ni²⁺, Mn²⁺, Cr³⁺, Zn²⁺ and Al³⁺, the solution (0.05 ml), two or three drops of saturated NH₄SCN soln. and two or three drops of acetone are passed successively through a micro-column of Al₂O₃. With ≤ 0.4 μ g of Co, a blue ring appears in 5 to 7 min. in neutral solution and in 10 to 12 min. in acid solution. In neutral solution, Fe³⁺ do not interfere, but in acid solution a red coloration is given. This interference can be prevented by using a column of Al₂O₃ and NaF in the ratio 1:8 to 1:10. The concn. of HCl can be 2%, but the minimum amount of Co detectable is 1.5 μ g. G. S. SMITH

1104. New indicator—oxine blue. I. E. Lev (Dnepropetrovsk Metallurgical Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 359-360.—The synthesis and use of a new acid-alkali indicator—5-p-diethylaminophenylimino-5:8-dihydro-8-hydroxyquinoline (oxine blue)—are described. The pH range is 3.90 to 5.50, the colour change is from orange in acid solution to blue in alkaline solution, and salt and temperature effects are insignificant. The indicator is used in ethanol solution. G. S. SMITH

1105. Chelatometry. X. Eriochrome red B. A new pM indicator. P. Wehber (Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1956, **153** (4), 253-261.—The use of Eriochrome red B (**I**) as an indicator in the complexometric titration of Zn, Pb and Cu is described. In the titration of Zn with EDTA at pH 10, the interference of Mg and Ca may be overcome by the addition of NH₄F, and that of Ba by (NH₄)₂SO₄.

in the titration at pH 6.5, Cu²⁺ interfere, but the addition of thiourea will complex small amounts (up to 12 mg) and will also overcome the interference of Pt⁴⁺ and Pd²⁺. The interference of Fe³⁺ is prevented by the addition of NH₄F and NaCl, but Al³⁺, Ti⁴⁺, Cd²⁺, Mn²⁺, Pb²⁺, Co²⁺ and Ni²⁺ interfere. Lead may be titrated with EDTA at pH 10, with **I** as indicator, a Na acetate buffer and Na K tartrate to prevent pptn. of Pb(OH)₂. The endpoint is sharp; Ca and Mg interfere, but small quantities of Ba do not interfere if NH₄F is added. The interference of a number of metals can be prevented by the addition of KCN. **I** is less suitable for the titration of Cu, as the colour change is not as marked and is masked by the blue of the Cu-EDTA complex. The titration may be done at pH 2 or, if ethanol is added, at pH 4.

P. S. STROSS

1106. Compleximetric titrations. (Chelatometry.) XIX. Bromopyrogallol red as compleximetric indicator. A. Jeníčková, V. Suk and M. Malát (Inst. Anal. Chem., Charles Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 760-764.—Bromopyrogallol red (dibromopyrogallol sulphone-phthalein) (**I**) has been found to be a suitable indicator for direct compleximetric titrations. **I** forms red complexes in acid medium, and violet or blue complexes in alkaline medium, with many metals (Pb, Bi, Hg, Cu, Cd, Sb, Sn, Tl, Al, Ni, Co, Zn, Mn, Ca, Sr, Ba, Mg, U, Mo, Th, Ti, Zr and some rare earths). Conditions are given for the direct compleximetric determination of Bi in acid soln. of Ni, Co, Cd, Mg and Mn in ammoniacal buffered soln., and of some rare earths in Na acetate medium. *Procedure for rare earths*—To a slightly acid soln. of the sample, containing 1 to 100 mg of the element (La, Ce, Pr, Nd, Sm, Y, Er) in 100 ml, add 15 drops of the indicator soln. (0.05% in 50% ethanol), aq. NH₃ until a blue or violet colour is produced and then Na acetate (1 to 2 g); titrate with EDTA till the colour changes to red. When titrating Ce, ascorbic acid must be added to prevent oxidation to ceric salt. J. ZÝKA

1107. Analysis for industry [primary standards in microvolumetric analysis]. M. Williams. *Ind. Chem. Mfr.*, 1956, **32**, 442-444.—The use of K₂CO₃, borax, K H phthalate and potassium di-iodate as primary standards is reviewed from recent literature. (18 references.) S.C.I. ABSTR.

1108. Ion screens. Capillary properties of differently cross-linked synthetic-resin-based anion exchangers. E. Blasius, H. Pittack and M. Negwer (Univ. Berlin-Chorlottenburg, Germany). *Angew. Chem.*, 1956, **68** (21), 671-677.—In order to determine the limits of the possibility of application of ion exchangers for the separation of ions of different sizes, the capillary properties of strongly basic anion-exchangers and also of a highly acid cation-exchange resin have been investigated. The variabilities of resin-pore structures and the distributions of platinum aggregates resulting from saturation of the resins with the hexachloroplatinate^{IV} complex were studied by means of the electron microscope. An apparatus and technique are described for establishing hydration and dehydration isotherms for different resins. Finally a method of separation and determination of milligram amounts of Mo and W is described in which the easy formation of the relatively large tungstoborate ion, which is not held by the resin, but passes to the filtrate, is utilised. Tungstoborate ion is

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2.—INORGANIC ANALYSIS

[Abstr. 1109-1116]

formed in the presence of molybdate by the addition of boric acid and Na acetate to the test soln. at pH 5.8. The aq. soln. of the cryst. slurry is adjusted to 5 N with HCl. This soln. is passed through a column 20 mm in diam. containing 60 to 65 ml of Permutit-ES fine-porosity resin (Cl form) at 2 ml per min., and the tungstoborate ions are eluted from the column with 50 ml of 5 N HCl. The W in the filtrate is determined as oxinate, with the method of Berg. After the determination of the sum of Mo and W by the same method, the Mo is obtained by difference. D. F. PHILLIPS

1109. Exchange spectrophotometry. I. W. J. Kirsten (Inst. Med. Chem., Univ. Uppsala, Sweden). *Mikrochim. Acta*, 1956, (11), 1617-1620 (in English).—Exchange reactions of the type $A + BC = AB + C$, where A is the component to be determined, BC and AB are slightly dissociated or sparingly soluble salts or complexes, and C absorbs light, can be used for the semi-direct spectrophotometric determination of traces of Cl^- , Br^- , F^- , S^{2-} , SO_4^{2-} , etc. It is necessary for the dissociation or solubility of BC to be much higher than that of AB, and the excess of BC used must not interfere with the measurement of C. The method is exemplified in the case $A = \text{Cl}^-$, $B = \text{Ag}^+$, $C = 1:2:3$ -benzotriazole. *Procedure*.—To the sample ($< 50 \mu\text{l}$ of 0.1 N soln.) add 10 ml of a mixture of ammonium acetate (0.5 g), zinc acetate dihydrate (2 g), water (5 ml), glacial acetic acid (5 ml), ethanol (180 ml) and ethyl acetate (100 ml) and shake for 1 min. with Ag 1:2:3-benzotriazole (10 mg). Centrifuge, dilute a 5-ml aliquot with 5 N aq. NH_3 to 25 ml and measure the extinction at $274 \text{ m}\mu$ in 1-cm cells.

A. R. ROGERS

2.—INORGANIC ANALYSIS

1110. Cementation [phase-exchange] of certain metals with zinc amalgam. E. F. Speranskaya (S. M. Kirov Kazakh State Univ.). *Zhur. Anal. Khim.*, 1956, 11 (3), 323-328.—Cadmium and Sb are quantitatively extracted from chloride, sulphate and ammoniacal solutions by zinc amalgam; Pb is quantitatively extracted from chloride and ammoniacal solutions; and Ni from ammoniacal solutions. Copper can be extracted quantitatively only when the amount of Zn used is not less than three times that of the Cu. Measurement of the potential during the process can be used to show the presence of chemical compounds, e.g., Zn_2Cu and ZnCu , in the amalgam. G. S. SMITH

1111. The use of some thioglycollanilides in inorganic analysis. I. R. N. Misra and S. S. Guha Sircar (Mayurbhanj Chem. Lab., Ravenshaw Coll., Cuttack, India). *J. Indian Chem. Soc.*, 1955, 32 (2), 127-134.—Ten thioglycollanilides have been synthesised from aromatic primary amines. Insol. complexes were formed with Ag, Pb, Hg^+ , Hg^{2+} , Cu, Cd, Bi, Sn, Zn, Co and Ni. Gravimetric determinations of Co with five compounds and of Ag with one compound have been carried out.

II. R. C. Swain, R. N. Misra and S. S. Guha Sircar, *Ibid.*, 1956, 33 (5), 329-334.—Nine further thioglycollanilides have been studied. Insol. complexes were formed with the same metal ions. Gravimetric methods are described for the determination of Ag with four reagents and of Co with three reagents. I. JONES

1112. The determination of impurities in high-purity metals by radioactivation. Yu. V. Yakovlev. Report of Symposium: "Issledov. Obl. Geolog., Khim. Metallurg. M., Izdat. Akad. Nauk, SSSR," 1955, 90-104; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,101.—The accuracy and sensitivity are studied of the radioactivation analysis of small amounts of elements in various substances, in those cases when direct determination without chemical separation is impossible. The possibility of achieving max. sensitivity, calculated theoretically for the determination of the element in a pure form and in the analysis of samples of complex composition, is examined. Appended are examples of the use of the radioactive determination of the rare-earth impurities in graphite, beryllium, bismuth and copper, zinc and lead, and also the rare earths, Sb, Mo, Cu and Zn in germanium. C. D. KOPKIN

1113. The thermal decomposition of some metal chelates of 5:7-di-iodo-8-quinolinol [8-hydroxy-5:7-di-iodoquinoline] (iodoxine). W. W. Wendlandt (Texas Tech. Coll., Lubbock, Texas, U.S.A.). *Anal. Chim. Acta*, 1956, 15 (6), 533-537.—Thermogravimetric studies of the chelates of 8-hydroxy-5:7-di-iodoquinoline (**I**) with Cu^{2+} , Ni, Fe^{3+} , La, Sc, U^{4+} and Th show that these complexes vary greatly in stability; the least stable (that of La) begins to decompose at 65° and the most stable (that of Cu^{2+}) at 165° . The oxide levels (i.e., const. wt.) are attained between 410° and 668° . These chelates can be prepared by adding a slight excess of a dil. soln. of **I** in dioxan to a dil. soln. of the metal salt in 2 N ammonium acetate soln.

W. J. BAKER

1114. Chelatometry. IX. The calculation of apparent stability constants of the metal complexes. A contribution to the Yatsimirskii theory. P. Wehber (Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1956, 153 (4), 249-253.—The stability constant of simple 1:1 metal chelates having a base as ligand can easily be calculated by using the Yatsimirskii theory (*Anal. Abstr.*, 1955, 2, 2942). A table giving stability constants at different pH values for a number of metals is included. P. S. STROSS

1115. Paper chromatography of inorganic ions. XV. R_F values in mixtures of butanol and hydrobromic acid. S. Kertes and M. Lederer (Inst. du Radium, Paris, France). *Anal. Chim. Acta*, 1956, 15 (6), 543-547.—The R_F values of 54 inorganic ions, determined by ascending paper-chromatography on Whatman No. 1 filter-paper developed with butanol - 10% aq. HBr (10:1 to 6) for ≈ 16 hr., are listed. In comparison with similar mixtures of butanol and HCl, a more efficient extraction of Cu^{2+} , Te^{4+} , Pb^{2+} , Rh^{3+} and In^{3+} is obtained. A few separations of certain elements are indicated. The data apply to 1% soln. of the bromide of each ion.

W. J. BAKER

1116. Separation of magnesium, aluminium, chromium, manganese, iron, nickel and copper by ion exchange. D. I. Ryabchikov and V. F. Osipova (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1956, 11 (3), 278-285.—To separate Cu, Al and Mg, the soln. is treated with $\text{Na}_2\text{S}_2\text{O}_3$ soln. until it is colourless and passed through a column of cationite (KU-2) (Na form); Al and Mg are retained and Cu passes through as $\text{Cu}(\text{S}_2\text{O}_3)_2$. Treatment of the column with 5% NaOH soln. sets free the Al

and further treatment with 4 N HCl yields the Al. To separate Cr and Fe, (a) the soln. is heated with NH₄SCN soln. and passed through the column in the H form; the Fe, which is retained, is extracted with 4 N HCl; or (b) the soln. is treated with Na₄P₂O₇, and at a pH of 1 to 3 is passed through the column in the Na form, and the Cr, which is retained, is then washed through with 10% H₂SO₄. To separate Mn and Fe, the soln., pH 2 to 3 after treatment with Na₄P₂O₇, is passed through the column in the Na form and the retained Mn is extracted with 10% H₂SO₄. To separate Cr and Mn, the column in the Na form is used either with the thiocyanates (Mn is retained) or the pyrophosphates (Mn is retained). To separate Fe, Cr and Mn, Na₄P₂O₇ is added and the Cr and Mn, which are retained on a column and then washed through with acid, are separated in thiocyanate soln. To separate Cr and Ni, a thiocyanate soln. is also used (Ni is retained).

G. S. SMITH

1117. Micro-flotation method of analysis of heavy water. I. P. Gragerov (L. V. Pisarzhevskii Inst. of Phys. Chem., Acad. Sci., Ukr.S.S.R.). *Zhur. Anal. Khim.*, 1956, **11** (3), 264-268.—An improvement of the method of Gilfillan and Polanyi (*Z. phys. Chem.*, 1933, **166**, 254) is described.

G. S. SMITH

1118. Some techniques in the assay of tritium. T. E. Banks, J. C. Crawhall and D. G. Smyth (Dept. of Physics, Med. Coll. of St. Bartholomew's Hosp., London). *Biochem. J.*, 1956, **64** (3), 411-416.—A method is described for the determination of ³H in infinitely thick solid samples in a windowless flow-type counter. With this apparatus the observed count rates of ³H-labelled compounds are directly proportional to their specific activities, provided that the samples are rendered electrical conductors by first mixing them with graphite. The ratio between the observed count rate and the specific activity is not significantly affected by an Ag atom in the mol. of the compound. The method of White *et al.* (*Brit. Abstr. C*, 1951, 241), in which ³H is assayed as methane, is modified so as to allow analysis on much smaller amounts of material and to measure quant. the vol. of methane obtained.

J. N. ASHLEY

1119. Thiocyanate interference in the permanganometry of hydrogen peroxide. B. R. Sant (Benares Hindu Univ., India). *Anal. Chim. Acta*, 1956, **15** (5), 413-414.—Thiocyanate interferes in the titration of H₂O₂ with KMnO₄, but this interference can be eliminated by the previous pptn. of the SCN⁻ with AgNO₃ in excess, the soln. being acidified with 2 N H₂SO₄. The titration is then carried out in the presence of the ptdt. AgSCN.

W. C. JOHNSON

1120. Contribution to the theory of paper chromatography of inorganic compounds. II. Semiquantitative micro-determination of sodium and potassium. J. Vavruch, M. Hejtmánek and J. Bouzková (Inst. Phys. Chem., High School of Chem. Technol., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (12), 1782-1785.—A simple chromatographic method for the semi-quant. determination of Na and K in mixtures, by a single procedure, was worked out. The method is suitable for the determination of 15 µg of K in the presence of 800 µg of Na, or 6 µg of Na in the presence of 700 µg of K. The whole procedure needs only 5.5 hr. and not more than 0.1 ml of the dissolved sample. The mean error amounts to ± 15 µg for K and ± 20 µg for Na. Calcium, Ba, Sr, Mg and ammonium

salts, sulphates and phosphates must be first removed and K and Na must be present in the form of chlorides. Lithium behaves similarly. The proposed method was tested by analysing the ash of biological material.

J. ŽYRA

1121. Determination of potassium by a tetraphenylborate method. R. M. Engelbrecht and F. A. McCoy (Res. Dept., Lion Oil Div., Monsanto Chem. Co., El Dorado, Ark., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1772-1773.—To a soln. containing > 45 mg of K⁺ and > 150 mg of NH₄⁺ is added 130 ml of 37% aq. formaldehyde, followed by 6 g of NaOH. While hot, the soln. is treated with 50 ml of 1% Na tetraphenylboron, and after cooling is filtered. The residue is dried at 110° and weighed. Results are compared with those of the chloroplatinate method, which leads to slightly higher figures.

D. A. PANTONY

1122. The colorimetric determination of traces of rubidium and caesium. A. I. Cherkesov, *Uch. Zap. Saratov. Univ.*, 1955, **42**, 85-91; *Ref. Zhur. Khim.*, 1956, Abstr. No. 36,143.—Hexanitrohydrazobenzene (**I**) is used as the reagent for the colorimetric determination of traces of Rb and Cs. To 1 ml of sample add 3 ml of reagent (an aq. soln. of the monosodium salt of **I** saturated at 18° to 20°); after 1.5 hr. filter off the ppt. with glass filter No. 4, dissolve it in 2 to 3 ml of acetone, wash the filter through with alcohol, and dilute the soln. to 20 ml. To 5 ml add 5 ml of water, and measure the extinction with filter S50, with water as comparison soln. Calibration curves have been constructed for determining Rb and Cs, and it is established that the relationship between extinction (E) and the concn. of Rb or Cs, in µg (C), is linear, and may be expressed by the equations C = 294·1E - 50·6 for Rb, and C = 236·4E - 58·2 for Cs. The presence of Li, Ca, Sr, Ba and Mg, and of Na in moderate amounts, has little influence on the accuracy. By the described method, 10 to 130 µg of Rb or Cs can be determined with an error of ± 3 µg.

C. D. KOPKIN

1123. The rapid determination of radioactivity due to caesium-137 in mixed fission products by anion exchange and gamma-ray spectrometry. J. L. Woodhead, A. J. Fudge and E. N. Jenkins (A.E.R.E., Harwell, Berks., England). *Analyst*, 1956, **81**, 570-577.—The use has been investigated of anion-exchange resins as solid precipitants in the analysis of mixed fission-product soln. for ¹³⁷Cs. An aliquot of the soln. of the fission product is adjusted to pH 1, specified amounts of caesium, ruthenium, zirconium and barium carriers are added and the mixture is run through a De-Acidite FF column in the carbonate form and the eluate is collected. The ¹³⁷Cs is in equilibrium with a short-lived daughter ¹³⁷Ba, and the activity of this is measured on a gamma-scintillation spectrometer. Results are as accurate as those obtained by a classical complete radiochemical separation.

A. O. JONES

1124. 3- and 5-Oximinomethylsalicylic acids as analytical reagents [for copper]. A. K. Ray and P. Ray (Dept. of Inorg. Chem., Indian Ass. Cult. Science, Calcutta). *Sci. & Cult.*, 1956, **21** (9), 547.—Both 3- and 5-formylsalicylic acids have been prepared by Duff's method of synthesis of hydroxyaldehydes (*J. Chem. Soc.*, 1932, 1987); the corresponding oximinomethylsalicylic acids were prepared

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from the two aldehydo acids by reaction with hydroxylamine. It is found that 3-oximinomethyl-salicylic acid can be used as a reagent for the gravimetric determination of Cu, as the copper salt $[\text{Cu}(\text{C}_8\text{H}_6\text{O}_2\text{N})_2]$ is pptd. completely in fairly acid medium; the ppt. can be weighed directly after being dried at 100° to 110° for 1 hr. Copper can be estimated in this way in the presence of the common metal ions, except those of Th and Zr, which are completely pptd. at pH 2; ter- and quadri-valent Ce and also La are pptd. in almost neutral soln. Under ordinary conditions, Cu can be determined accurately in quantities of the order of 0.001 g.

P. HAAS

1125. Use of 3-hydroxy-2-naphthaldehyde in analytical chemistry. II. New gravimetric semimicro method for determining copper. S. I. Gusev and V. I. Kumov (Molotov Medicinal Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 303-306.—To determine Cu in brass, the sample (0.1 g) is dissolved in conc. HNO_3 and aq. NH_3 is added; any ppt. is filtered off and washed with water. The filtrate is diluted to 100 ml in a calibrated flask and 5 ml, mixed with 3 ml of 95% ethanol and 1 ml of 25% aq. NH_3 , is boiled and treated with 6 ml of a 2% soln. of 3-hydroxy-2-naphthaldehyde. The pptd. copper complex is collected after 25 to 30 min. in a filtering crucible, washed with water and then dried at 115° to 120° . In alloys containing Al, Fe and Cr, interference is prevented by means of tartaric acid. Nickel, if present, must be removed by means of dimethylglyoxime. To determine Cu in malachite and copper-bearing sandstone, the sample (0.1 to 0.2 g) is dissolved in HNO_3 , insol. matter is filtered off and the filtrate is diluted to 100 ml. A 10-ml aliquot is mixed with 1 to 3 ml of 10% tartaric acid soln., and then with 5 ml of ethanol and 3 ml of 25% aq. NH_3 . The boiling liquid is treated with 15 ml of the reagent soln. and filtered after 25 to 30 min.

G. S. SMITH

1126. A new method for the iodometric determination of copper and lead. K. B. Yatsimirskii and E. N. Roslyakova. Report on Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 124-127; *Ref. Zhur. Khim.*, 1956, Abstr. No. 29,305.—The method is based on the formation of the almost insol. complexes $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{S}_2\text{O}_3)_3]_2 \cdot 12\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_6]_2[\text{Pb}(\text{S}_2\text{O}_3)_3]$, obtained by pptn. of salts of Cu and Pb with $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in the presence of excess of $\text{Na}_2\text{S}_2\text{O}_3$. To 5 ml of the weakly acid 0.05 to 0.1 M soln. of the copper or lead salt add 20% ammonium acetate soln. (5 ml), 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ (25 ml), and excess of a saturated soln. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (15 to 20 ml). Make up to 100 ml, mix, and filter through a dry filter into a dry flask. Titrate an aliquot (20 ml) with 0.02 to 0.04 N iodine to determine the excess of $\text{Na}_2\text{S}_2\text{O}_3$. No interference is caused by Al, Cr, Fe, Ni, Co, Mn, Mg or Ca. The following precipitate together with Cu and Pb—Cd, Hg, Bi, Zn and Ag. The limiting permissible error (twice the mean-square error) for Cu is $\pm 0.4\%$ and for Pb $\pm 0.3\%$. The time for one determination is 20 to 30 min.

C. D. KOPKIN

1127. Titration of copper oxinate in glacial acetic acid. C. H. Hill, H. Tai, A. L. Underwood and R. A. Day, jun. (Dept. of Chem., Emory Univ., Emory, Ga., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1688-1689.—The 8-hydroxyquinoline complex is pptd. by standard methods and is then dissolved in glacial acetic acid (50 ml per 100 mg of complex).

Into the soln. is bubbled H_2S and the liberated 8-hydroxyquinoline is titrated potentiometrically with 0.1 N HClO_4 in glacial acetic acid. The precision is given as ± 0.5 mg.

D. A. PANTONY

1128. Chelatometry. XI. Nitrilotriacetic acid (NTA) as a standard solution. Estimation of copper at pH ≈ 9 . P. Wehber and W. Johannsen (Lab. Metallhütte Markt A.-G., Hamburg-Wilhelmsburg). *Z. anal. Chem.*, 1956, **153** (5), 324-327.—In the determination of Cu^{2+} , a solution buffered to pH ≈ 9 with aq. $\text{NH}_3 - \text{NH}_4\text{Cl}$ was titrated with 0.1 M nitrilotriacetic acid. With murexide as indicator, 12 to 60 mg of Cu was determined with a mean error of $\approx \pm 0.3\%$; with Ponceau 3R as indicator, 12 to 45 mg of Cu was determined with a mean error of $\pm 0.1\%$.

M. F. C. LADD

1129. Method of concentration of traces of copper by means of organic reagents. V. T. Chuiko and A. U. Mamenko (Cherkask Pedagogical Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 332-336.—When traces of Cu in a solution of $\text{Pb}(\text{NO}_3)_2$ are collected by co-pptn. with part of the Pb pptd. with 8-hydroxyquinoline, the proportion of Cu in the ppt. in relation to the total Cu becomes less as the total amount of Cu is progressively reduced below a certain limit. Thus the ppt. obtained from 8 ml of 0.1 M $\text{Pb}(\text{NO}_3)_2$, 1 ml of 2 M Na acetate and 0.5 ml of 0.15 M 8-hydroxyquinoline contains 97 to 98% of the Cu when 80 μg is initially present, and only 24 to 34% when 5 to 10 μg is initially present. Complete extraction of the Cu can be attained in such cases when the 8-hydroxyquinoline complexes are extracted with CHCl_3 , followed by treatment of the extract with HNO_3 and extraction of Cu from the acid extract with dithizone. Copper can be extracted satisfactorily from salts of Cd and Pb by extraction of the diethyldithiocarbamate with CHCl_3 . This method applied to salts of Ni and Co is subject to errors—Cu is incompletely extracted and some of the Ni or Co appears in the CHCl_3 layer. Standards can be used to compensate for the errors.

G. S. SMITH

1130. The photocolorimetric determination of beryllium with thoron. L. P. Adamovich and A. P. Mirnaya. Report on Symposium: "Sovrem. Metody Anal. Metal.", M., Metallurgizdat, 1955, 172-175; *Ref. Zhur. Khim.*, 1956, Abstr. No. 25,936.—To 3 ml of soln. (pH ≈ 12) add 4 ml of a borate buffer soln. (pH 12.4) and 3 ml of thoron soln. (0.0426 g in 100 ml). Mix and pour into a 20-mm cell, and place the cell in the right-hand beam of the colorimeter; a green filter is used. The left-hand beam is left clear. Place the measuring drum on 100% transmission and adjust the galvanometer current to zero. Mix 7 ml of the buffer soln. and 3 ml of thoron soln. and measure the transmission of this blank in the right-hand beam. A calibration curve is obtained by measuring the transmissions of soln. with known amounts of Be. For each concn. take 16 to 20 readings. The method has been used for the determination of Be in aluminium salts. If the soln. is treated in the cold with excess of NaOH and the Be is determined in the filtrate, no interference is caused by 200-fold excess of Al^{3+} , Fe^{3+} and Mn^{2+} . Magnesium interferes in 200-fold excess, but does not interfere in concn. commensurate with that of Be. Interference is caused by Zn, Ca and Cu if these are present in concn. equal to that of Be.

C. D. KOPKIN

1131. A new rapid method for the determination of beryllium in beryl. A. K. Sen Gupta (Inorg. Chem. Lab., Univ. Coll. of Science, Calcutta). *Sci. & Cult.*, 1956, **21** (11), 687-688.—Beryl is completely disintegrated by Na fluoroborate above 540°, and Fe and Al are separated as insol. complex fluorides. The Be is determined as Ba fluorobérylate.
P. HAAS

1132. Determination of beryllium in titanium alloys. L. C. Covington and M. J. Miles (Titanium Metals Corp. of America, Henderson, Nev., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1728-1730.—The sample, containing 0·25 to 1% of Be, is dissolved in dil. HCl or H₂SO₄ and to the soln., or an aliquot, is added an excess of H₂O₂, and the pH is adjusted to 5·5 with dil. NaOH in the presence of EDTA (tetrasodium salt). After the addition of buffer (sodium borate - NaOH - citric acid), a soln. of 4-(*p*-nitrophenylazo)orcinol is added. The intensity is measured at 515 m μ *vs.* a reagent blank; the concn. of Be is derived by reference to an almost linear calibration curve. A standard deviation of $\pm 0\cdot006\%$ in the range quoted is given. Metals normally present in titanium alloys do not interfere, but F⁻ and BF₄⁻ prevent colour development.
D. A. PANTONY

1133. Inorganic chromatography. I. Chromatographic separation of beryllium, uranium and titanium. J. Michal (Res. Inst. Ores, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (4), 542-546.—In this paper-chromatographic method, a mixture of isopropyl alcohol, acetylacetone and HCl was used as solvent. After separation, the ions were detected with an ethanolic soln. of querectin and a soln. of K₄Fe(CN)₆. The planimetric method was used for the quant. evaluation of separated spots. Small amounts of Fe and Al and Sn and Sb do not interfere. *R_F* values for Be, U and Ti are given. In the analysis of mixtures of Be and U in various proportions (10 to 90 μ g of Be + 12 to 120 μ g of U) the average error did not exceed $\pm 10\%$.
J. ZÝKA

1134. The determination of calcium in magnesium alloys. R. S. Volodarskaya and G. N. Derevyanko. Report of Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 190-193; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,311.—To the sample of alloy (1 g) add water (15 ml) and dil. H₂SO₄ (1:5) (15 ml); to the resulting soln. add aq. NH₃ (150 ml) (free from ammonium carbonate) and boil for 15 min. Filter and wash the ppt. with hot 2·5% aq. NH₃. Evaporate the filtrate to 100 ml and determine the Ca as oxalate. C. D. KOPKIN

1135. The solubility of calcium and magnesium hydroxyquinolates. A. A. Popel' and A. V. Gladkova. *Uch. Zap. Kazansk. Univ.*, 1955, **115** (3), 89-92; *Ref. Zhur., Khim.*, 1956, Abstr. No. 43,456.—The solubility of magnesium and calcium hydroxyquinolates was determined in aq. ethanolic solutions. It was found that the solubility of calcium hydroxyquinolate was two to three times that of the magnesium compound. In soln. containing 0·01 M CaCl₂, the solubility of the calcium compound was 30 to 40 times that of the magnesium compound in soln. containing 0·01 M MgCl₂.
R. LORD

1136. Precipitability of strontium oxalate in the presence of other ions. M. P. Babkin (Donetz Ind. Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 337-340.—In the presence of M KNO₃, M KCl and M

ammonium acetate the solubility of Sr oxalate is increased 6·4, 5·4 and 9 times, respectively.

G. S. SMITH

1137. The macro-, semi-micro and micro-determination of strontium with picrolonic acid. N. P. Pengev and D. Kh. Nonova. *Izv. Khim. Inst. Bulgar. Akad. Nauk.*, 1955, **3**, 53-68; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,149.—To the soln. of SrCl₂ (1·5 to 20 ml) containing 15 to 36 mg of Sr and heated to between 50° and 55°, add dropwise with continuous stirring 0·01 N picrolonic acid. Allow the ppt. to settle and cool in ice, and filter off in a crucible. Wash with ice water or CS₂, dry at room temp. in a stream of air and weigh. The ppt. has the composition Sr(C₁₀H₇O₅N₄)₈H₂O.
C. D. KOPKIN

1138. Phototurbidimetric titration methods. I. The system BaSO₄ - BaCl₂ - C₂H₅OH - H₂O; II. The system BaSO₄ - HCl - C₂H₅OH - H₂O; III. The system BaSO₄ - BaCl₂ - HCl - C₂H₅OH - H₂O. N. D. Podobed. *Nauch. Trudy Stalingrad Mekhan. Inst.*, 1955, **2**, 251-297; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,288.—I. The dependence of light absorption in the system BaSO₄ - BaCl₂ - ethanol - H₂O on the concn. of ethanol and the excess of the precipitant has been studied. The light absorption depends on the order of introducing H₂SO₄ and BaCl₂ into the system. It is established that copptn. of BaCl₂ with the BaSO₄ increases with the excess of BaCl₂. The possibility of using the pptn. of SO₄²⁻ with BaCl₂ in alcoholic soln. for the determination of H₂SO₄, with a calibration curve, is indicated. The most satisfactory results were obtained in the concn. range of 60 to 200 mg of SO₄²⁻ per litre.

II. The system BaSO₄ - HCl - ethanol - H₂O has been studied by measurement of the light absorption. It is found that, with increase of HCl in the system, the max. in the absorption curve is displaced towards the region of higher ethanol concn., because of increase of the solubility of BaSO₄ in the presence of HCl.

III. The dependence of the light absorption in the system BaSO₄ - BaCl₂ - HCl - ethanol - H₂O on the content of ethanol and HCl in the presence of a const. (0·3 mole per litre) excess of BaCl₂ has been studied. It is shown that, with increase of the excess of HCl in the system, the max. absorption increases, moving towards the region of greater ethanol content.
C. D. KOPKIN

1139. Separations involving sulphides. I. Separation of selenium, arsenic, antimony and mercury from barium. I. K. Taimni and M. N. Srivastava (Univ. of Allahabad, India). *Anal. Chim. Acta*, 1956, **15** (6), 517-520.—The separation of Se, As, Sb or Hg from Ba can be made by adding an excess of 2 N aq. Na₂S soln. and then decomposing the thio salt with HCl to precipitate the sulphide of Se, As, Sb or Hg. The ppt. is washed, dried for 1 hr. at temp. between 95° and 110°, and weighed. The Ba in the filtrate can be determined as BaSO₄. When decomposing the thio salt, the concn. of the HCl should be N for the separation of Se, 6 N for As, and dil. for Sb or Hg. The accuracy is high. (Cf. Taimni and Salaria, *Anal. Abstr.*, 1956, **3**, 323.)
W. J. BAKER

1140. The determination of zinc in wood-preserving solutions. W. J. Wilson (Dominion Lab., Auckland, New Zealand). *Anal. Chim. Acta*, 1956, **15** (6), 508-510.—In the procedure described,

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2.—INORGANIC ANALYSIS

[Abstr. 1141-1148]

Cr is removed by extraction with isobutyl methyl ketone in HCl (1 + 1). Cu is then pptd. with cupferron, and the Zn in the filtrate is titrated with standard $K_4Fe(CN)_6$ soln., with *o*-dianisidine as indicator. The accuracy is high. W. J. BAKER

1141. Micro-heterometric determination of traces of zinc in solutions and alloys with sodium diethyl-dithiocarbamate. M. Bobteisky and R. Rafailoff (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **15** (5), 457-464.—Zinc is titrated heterometrically (*Anal. Abstr.*, 1956, **3**, 12) in the presence of large excesses of Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , Al^{3+} , Cr^{3+} and Mn^{2+} . Errors from -1·2 to +0·4% are recorded. *Procedure*—To 20 ml of soln. containing 0·2 to 0·4 mg of Zn add 2 ml of 0·1 M acetic acid and titrate with 0·003 M Na diethyldithiocarbamate. When Mn^{2+} are present, the addition of K tartrate is necessary. W. C. JOHNSON

1142. Chemical determination of very minute quantities of zinc, copper and titanium in hard alloys. Z. I. Kardakova. *Sb. Statei Mosk. Vyssh. Tekhn. Uch.*, 1955, **36**, 30-36; *Ref. Zhur., Khim.*, 1956, Abstr. No. 39,872.—For the determination of Zn, 1 g of stellite (cobalt- or iron-base), is dissolved in HCl in the presence of an oxidising agent. Si and W are removed, the medium is made weakly acid and diluted to 50 ml. To 5 ml of the soln. is added 5 ml of a 20% soln. of NaOH or 1 to 1·5 ml of aq. NH_3 . The ppt. is filtered off and washed with aq. NaOH or NH_3 to a fixed volume of filtrate (10 ml), then 1·5 g of NH_4Cl and \approx 0·5 g of Na_2SO_4 are added and the soln. is polarographed at 3·8 V. For iron-base stellite, the mercuric thiocyanate method is applied for the determination of Zn. Copper is pptd. by H_2S from the soln. obtained after the removal of W, the ppt. is dissolved in HNO_3 and the Cu is removed by micro-electrolysis in the presence of H_2SO_4 . In cobalt-base stellites, Cu is determined by electrolysis after fusing the sample with Na_2CO_3 and extracting the melt with water. Titanium is separated as the cupferron complex, the ppt. is fused with $K_2S_2O_8$, and extracted with H_2SO_4 ; Fe is removed by electrolysis at a mercury cathode and the determination is completed colorimetrically with H_2O_2 . Titanium is adsorbed by the ppt. of H_2WO_4 and is determined after fusing the ppt. with fusion mixture. G. BREWER

1143. Potentiometric titration of cadmium with potassium ferrocyanide. A. Basiński and W. Bogotko (Toruń Univ., Poland). *Roczn. Chem.*, 1956, **30** (2), 613-618.—The neutral or weakly acid solution is titrated with standard $K_4Fe(CN)_6$ in the presence of $(NH_4)_2SO_4$. Cations that give sparingly sol. ferrocyanides, such as those of Zn, Pb or Cu, interfere. R. TRUSCOE

1144. The polarographic determination of cadmium and zinc in copper ores. D. P. Shcherbov and E. P. Guzhova. Report of Symposium: "Sovrem. Metody Anal. Metall. M. Metallurgizdat," 1955, 154-159; *Ref. Zhur., Khim.*, 1956, Abstr. No. 32,761.—Dissolve the ore in acid and evaporate the soln. to dryness. Dissolve the residue in 20 ml of HCl (1:40), introduce a spiral of lead strip (thickness \approx 1 mm, width 1 to 1·5 cm, length 10 to 15 cm), and heat to boiling-point. After 20 to 25 min. remove the spiral, wash it with water, place it in hot HNO_3 to dissolve Cu, wash with water, once more place it in the soln. to be analysed, and warm for a further 20 min. After deposition has finished, remove the spiral and rinse it with water. To

oxidise Fe^{2+} , add to the soln. two to three drops of 30% H_2O_2 , boil till the H_2O_2 is decomposed and evaporate to 10 ml. Dilute the cold soln. to 50 ml with the background soln. (*N* NH_4Cl and 3*N* aq. NH_3), allow the ppt. to settle, and make a polarographic determination at potentials of -0·7 and -1·1 V. With a high concn. of Cu, the spiral is first immersed in the soln. in the cold, and renewed as soon as it is covered with a layer of Cu; the final deposition is carried out by heating. In determining Zn, the Cu is removed in the same way by deposition on lead. Polarography is carried out at potentials of -1·3 and -1·6 V. C. D. KOPKIN

1145. Polarographic determination of cadmium in pig-lead. P. N. Kovalenko and T. S. Dolzhenko. *Uch. Zap. Rostovsk. n/D. Univ.*, 1955, **25**, 57-64; *Ref. Zhur., Khim.*, 1956, Abstr. No. 43,503.—The sample of lead (100 g) is dissolved in H_2O (640 ml) and conc. HNO_3 (160 ml); the soln. is cooled and conc. H_2SO_4 (31 ml) is added. After filtering, the filtrate is evaporated to 150 ml and the Pb is determined by electrolysis. Sodium citrate soln. (0·060 M) (pH 4) is added to the soln. obtained after electrolysis and the Cd is determined polarographically. R. LORD

1146. 5:6-Benzoinquinolinic acid as an analytical reagent. III. Determination of mercury. Anil Kumar Majumdar and Siddheswar Banerjee (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1956, **15** (6), 511-513.—Mercury can be determined gravimetrically by pptn. with a 1% aq. soln. of the sodium salt of 5:6-benzoinquinolinic acid at pH 1·9 to 6·0 and 100°. The mercury complex is washed with H_2O , dried at 110° and weighed as the anhyd. salt (stable up to 150°). Provided that tartaric acid is added and the soln. is acidified with dil. HNO_3 or acetic acid before the addition of the reagent, the pptn. can be made in the presence of ammonium salts, salts of alkali and alkaline-earth metals, rare earths, Mg, Cr, Fe, Al, Th, Ti, Zr, UO_4^{2-} , Pb, Bi, and SO_4^{2-} , NO_3^- , MoO_4^{2-} , VO_4^{2-} , WO_4^{2-} , AsO_4^{3-} and PO_4^{3-} . W. J. BAKER

1147. Determination of mercury via reduction with hydrazine. J. J. Lingane and R. S. Kline (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (5), 410-413.—The method described is applicable to the determination of Hg in the presence of Cd, Pb, Cu, Bi, Sn, As and Sb. The errors obtained in the presence of these metals range from -0·9% to +0·5%. *Procedure*—Dissolve the sample, containing up to 0·2 g of Hg, in 8 ml of hot 6*M* HCl, adding, if necessary, 0·5 ml of conc. HNO_3 . Add a soln. of 2 g of Na tartrate in 20 ml of 7*M* aq. NH_3 , cool to below 35° and add 5 ml of 0·2*M* hydrazine sulphate. Set aside until no more pptn. takes place (\approx 30 min.), centrifuge and wash the pptd. Hg until free from Cl^- . Dissolve the Hg in 1 to 2 ml of conc. HNO_3 , dilute to 10 ml with water, boil off oxides of nitrogen, dilute to 50 ml, cool to < 20°, add 1 ml of 0·3*M* ferric alum or nitrate and titrate with 0·05*M* KSCN. W. C. JOHNSON

1148. The colorimetric determination of mercury with methyl violet. M. P. Anan'evskaya and V. I. Petrashev. *Nauch. Trudy Novocherkas. Politekhn. Inst.*, 1955, **26**, 246-251; *Ref. Zhur., Khim.*, 1956, Abstr. No. 25,960.—A colorimetric method is described in which Hg is determined by addition of methyl violet in the presence of KI at pH 1·4, the colours being visually compared. C. D. KOPKIN

2.—INORGANIC ANALYSIS

1149. Quantitative determination of mercuric chloride and sodium chloride when present together. A. A. Medvedovskii. *Apteknnoe Delo*, 1956, 5 (4), 44-48.—For the determination of $HgCl_2$, a soln. of the sample is titrated against 0.1 N NaOH in the presence of acetone and thymolphthalein. The mercury forms a colourless soluble compound with the acetone; at the end of the titration the soln. should contain 15 to 25% of acetone. A blank experiment is carried out at the same time. Total chloride is then determined argentimetrically with K_2CrO_4 as indicator, and the amount of NaCl is found by difference. The method can be applied to tablets.

E. HAYES

1150. Determination of traces of mercury in mercury-ore ash by catalytic action of mercuric ions. S. Asperger and D. Pavlović (Inst. of Inorg., Anal. and Phys. Chem., Fac. of Pharm., Univ. of Zagreb, Croatia, Yugoslavia). *Anal. Chem.*, 1956, 28 (11), 1761.—The mercury-ore ash (0.2 to 0.6 g) is heated under air at 120° and the issuing gases are mixed with bromine gas and absorbed in bromine water. The soln. is allowed to react with a mixture of $Fe(CN)_6^{4-}$ and nitrosobenzene. The absorption of the colour of the violet complex is measured at 528 m μ and the concn. of Hg is derived from a given formula, allowance being made for Hg in the atmosphere. In the range 0.0024 to 0.0097% of Hg, the standard deviation was 0.00015%.

D. A. PANTONY

1151. Boron hydride monitoring devices employing a triphenyltetrazolium chloride reagent. L. J. Kuhns, R. H. Forsyth and J. F. Masi (Calloway Chemical Co., Callery, Pa., U.S.A.). *Anal. Chem.*, 1956, 28 (11), 1750-1752.—Two experimental instruments for monitoring atmospheres are described: a portable field model and an automatic differential reflectance photometric analyser. Both depend on the non-specific, highly sensitive reduction of a triphenyltetrazolium chloride reagent by boron hydrides to give a red coloration. The field model can detect 0.1 p.p.m. of decaborane and 0.5 p.p.m. of pentaborane, and the automatic instrument is capable of detecting 0.1 p.p.m. of either compound.

E. G. CUMMINS

1152. Potentiometric method for the determination of aluminium on a semi-micro scale. J. R. McCallum (Quebec North Shore Paper Co., Baie Comeau, Que., Canada). *Canad. J. Chem.*, 1956, 34 (7), 915-920.—The method for determination of Al by titration with NaF, with a ferri-ferrous half-cell, as originally proposed by Treadwell and Bernasconi (*Helv. Chim. Acta*, 1930, 13, 500), has been modified for semi-micro applications and used for analysis of pulp and paper ash.

S.C.I. ABSTR.

1153. Sodium gluconate as a complexing agent in the volumetric analysis of aluminium compounds. H. L. Watts and D. W. Utley (Alcoa Res. Lab., Aluminum Co. of America, East St. Louis, Ill., U.S.A.). *Anal. Chem.*, 1956, 28 (11), 1731-1735.—Of ten organic hydroxyl reagents examined, Na gluconate was found to be most suitable for the retention of Al^{3+} in soln., before neutralisation, in the titrimetric complex fluoride determination of Al. Procedures for the determination of total OH^- , CO_3^{2-} , HCO_3^- and H^+ in the presence of Al are described. Precision data for these are presented. Interference of 37 ions, most of which lead to high results, is discussed.

D. A. PANTONY

1154. Determination of alumina [inclusions] in aluminium metal. K. Kapitańczyk, Z. Kurzawa and M. Miedziński (Poznań Univ., Poland). *Roczn. Chem.*, 1956, 30 (2), 607-612.—About 1 g of powdered metal is dissolved in 100 ml of a solution containing 4 g of tartaric acid, 1 g of citric acid and 3 ml of saturated aq. $HgCl_2$, the vol. being kept constant. After the addition of 10 ml of HCl (1:1), the solution is boiled for 5 min., and filtered. The residue is washed ($\times 5$) with 5% aq. tartaric acid, and then with water, the drop of Hg on the filter is removed, and the filter is ignited with $K_2S_2O_7$. The product is dissolved in water, then 1 ml of HCl (1:25), 20 ml of ammonium acetate (40%), 4 ml of a solution of 5 g of Na_2CO_3 and 5 g of KCN in 90 ml of water, 10 ml of 0.1% haematoxylin soln., 4 ml of acetic acid (10%), and water to 100 ml are added, and the extinction is measured. The results apply to inclusions only; surface oxide films are dissolved together with the metal by the reagent.

R. TRUSCOE

1155. The determination of aluminium in alloys using cationites. A. I. Lazarev. Report of Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 182-184; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,320.—Stand the cationite SBS (N form) in water for 4 hr., transfer it to a column and treat with N HCl (200 ml) and water (150 ml). Dissolve the alloy (0.4 g) in HCl and HNO_3 (5 ml of each) and evaporate to dryness. Add 120 to 150 ml of water to the residue; when solution is complete, pass it through the column, at a rate ≥ 3.5 ml per min., and wash with 20 to 40 ml of water. Reject the eluate. Remove Al from the column by treatment with N NaOH (200 ml) and water (120 ml). Neutralise the eluate with conc. HCl, add 2 ml in excess and 10 ml of an 80% soln. of acetic acid. To remove Cu, add 6 g of $Na_2S_2O_3 \cdot 5H_2O$ to the acid soln., boil for 2 to 3 min. and filter. Wash the ppt. with hot dil. HCl (1:100) and reject the residue. Heat the filtrate to boiling-point, add a 10% soln. of $(NH_4)_2HPO_4$ (200 ml) and a 20% soln. of Na acetate (20 ml), and boil for 5 to 10 min. Filter off the ppt., wash it with hot 1% NH_4NO_3 soln., dissolve it in dil. HCl (1:1) (10 ml) and reprecipitate the Al. Ignite the ppt. at 1000° and weigh.

C. D. KOPKIN

1156. The volumetric determination of aluminium in the presence of magnesium, iron, copper, zinc and manganese. V. K. Zolotukhin and O. P. Dimerko. Report of Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 176-181; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,321.—The limiting concn. of Mg, Fe, Cu, Zn and Mn allowable in the determination of Al by the fluoride-tartrate method are determined. In the presence of $MgCl_2$, $FeCl_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $MnCl_2$ in the quantities 3 to 3.8; ≥ 1.0 ; ≥ 0.15 ; ≥ 0.08 and ≥ 0.06 moles, respectively, per mole of Al, the errors in the determination of Al are, respectively, -0.23, -0.75, -0.90, -0.78 and -0.90%. In the presence of 1 mole of aluminium salt, there should be present ≥ 1.5 moles of $MgCl_2$, 0.4 mole of $FeCl_3$, 0.56 mole of $Cu(NO_3)_2$, 0.03 mole of $ZnCl_2$ or 0.02 mole of $MnCl_2$; the error does not exceed 0.43%.

C. D. KOPKIN

1157. Polarographic determination of aluminium and zinc in magnesium alloys. D. G. Gage (Naval Res. Estab., Dartmouth, Nova Scotia, Canada). *Anal. Chem.*, 1956, 28 (11), 1773-1774.—The alloy is dissolved in dil. $HClO_4$ to give a concn. of Mg^{2+}

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of 5 mg per 50 ml of a soln. suitably buffered according to standard procedures. The soln. is examined polarographically under N. The wave at -0.5 V vs. the S.C.E. corresponds to the content of Al^{3+} , and that at -1.2 V to Zn^{2+} ; the concn. are derived by comparison with standards. A use of the method is illustrated.

D. A. PANTONY

1158. Photometric method for the determination of aluminium and iron in aluminite rocks. M. K. Akhmedli and È. A. Bashirov. *Uch. Zap. Azerb. Univ.*, 1955, (7), 25–29; *Ref. Zhur., Khim.*, 1956, Abstr. No. 39,834.—In the separation of Fe from Al (cf. Tartakovskii, *Zavod. Lab.*, 1940, **9**, 971), the substitution of the solvents amyl alcohol and ether by a mixture of *n*-butanol and ether (1:4) is recommended. Iron was determined in the extract by the thiocyanate method and Al in the residue by the alumino method. After the addition of a 10% solution of NH_4SCN , extraction was carried out with 10, 10 and 15 ml of the solvent mixture. The combined extracts were diluted to 50 ml with isoamyl alcohol and used for the absorptiometric determination of Fe. The aqueous layer was diluted to a vol. of 50 to 100 ml and to 1 ml of the solution so obtained were added 4 ml of acetate buffer (pH 4.4) and 0.1 ml of a 0.5% solution of alumino. The Al was determined absorptiometrically 10 min. after adding the reagents. In both cases the optimum wavelength was shown to be $533 \text{ m}\mu$. The mean error of the determination of Al and Fe is $+1.66$ and $+0.6\%$, respectively. The method is applied to samples decomposed by the soda method after the removal of SiO_2 .

G. BREWER

1159. The determination of aluminium and fluorine with stilbazo [ammonium 4:4'-di-(3:4-dihydroxyphenylazo)stilbene-2:2'-disulphonate]. V. A. Nazarenko and E. A. Biryuk. Report of Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 188–189; *Ref. Zhur., Khim.*, 1956, Abstr. No. 25,937.—To determine Al in the presence of F, to 1 ml of the neutral soln. containing $> 5 \mu\text{g}$ of Al and $> 10 \mu\text{g}$ of F, add 0.1 N HCl (0.1 ml), 0.1 ml of a soln. of Be (200 μg of Be per ml), 5% ascorbic acid soln. (0.15 ml), 2.5 ml of acetate buffer soln. (pH 5.4) and 0.01% aq. soln. of stilbazo (0.5 ml). Dilute to 5 ml, mix, and after 10 min. compare with a series of standards prepared similarly. The reaction of Al with stilbazo may be used as the basis of a method for determining F colorimetrically. To determine F, the concn. of Al must be known (determined as described above). To 1 ml of the neutral soln. containing $> 10 \mu\text{g}$ of F and $> 5 \mu\text{g}$ of Al, add 5 μg of Al as a soln. Add the 0.1 N HCl, the ascorbic acid soln., the acetate buffer soln. and the stilbazo soln. as in the determination of Al. It is not necessary to add the soln. of Be. Dilute to 5 or 6 ml if necessary, set aside for 10 min., and compare with a series of standards containing 5 μg of Al and 1 to 10 μg of F, treated in the same way.

C. D. KOPKIN

1160. Separation of indium and gallium by means of solvent extraction. H. Hartkamp and H. Specker (Inst. für Spectrochem., Dortmund-Aplerbeck, Germany). *Angew. Chem.*, 1956, **68** (21), 678.—It is shown that cyclohexanone is an especially suitable solvent extracting agent for the quantitative separation of In and Ga when present in KI soln. In contrast with the usual extraction procedures, only small concn. of halide are necessary. As the starting soln. are either neutral or only weakly acid,

subsequent operations are not interfered with. Results are tabulated which show that $\approx 10 \text{ mg}$ of Ga can be separated from 10, 20 and 50 mg of In. The Ga is in the aq. phase and the In in the cyclohexanone phase. A systematic loss of about 0.5% is indicated, and it is calculated that the separation factor (β) is $< 10^5$.

D. F. PHILLIPS

1161. Polarographic and oscilloscopic determination of indium in presence of cadmium. L. Treindl (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (4), 534–538.—A method has been developed for the direct polarographic and oscilloscopolarographic determination of traces of In in metallic Cd and its salts and for the determination of In in zinc in the presence of Cd. With 0.5 to 5 M soln. of KI as supporting electrolyte, In and Cd can be determined in the presence of each other; with 3 M KI as supporting electrolyte, In can be determined even in the presence of a 10,000-fold excess of Cd. In soln. of pH 2 to 3, at a temp. $> 5^\circ$, a polarographic and oscilloscopolarographic titration of In in the presence of Cd, with 0.01 to 0.1 M soln. of EDTA, can be carried out. When titrating $6 \times 10^{-3} \text{ M}$ soln. of In, an accuracy within ± 1 to 2% was achieved.

J. ZÝKA

1162. Chromotropic azo dyestuffs as reagents for tervalent thallium. I. M. Korenman, V. G. Potemkina and L. S. Fedorova (Gorki State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (3), 307–309.—Tervalent Tl gives colours with certain chromotropic azo dyes, e.g., 3-*p*-dimethylaminophenylazo-4:5-dihydroxynaphthalene-2:7-disulphonic acid, which is suitable for the colorimetric determination of 1 to 10 μg of Tl in 1 ml of solution, even in the presence of Al ($\times 100$ to 1000), Fe ($\times 100$), Mg ($\times 300$) and Ca ($\times 700$). The solution (1 ml) is mixed with 0.1 ml of 2 N acetic acid, four drops of glycerol and three drops of a 0.1% aq. soln. of the reagent. The blue colour of the reagent soln. becomes violet in the presence of Tl^{3+} . No reaction is given by Tl^{+} .

G. S. SMITH

1163. Determination of thallium in lead. E. N. Castells and A. H. Guerrero. *An. Asoc. Quim. Argentina*, 1956, **44**, 104–108.—Comparison of the determination of Tl in lead by pptn. of Tl alone (in the presence of ammonium acetate) or with PbI_2 followed by washing with ammonium acetate-acetic acid indicate that the former method is better and gives accurate results down to 0.4% of Tl in lead. The reaction is also suitable for the qualitative detection of Tl in lead, with a limit of 1 in 5×10^4 . The qualitative detection of Tl in lead by means of NaOH and H_2O_2 is sensitive to only 1 in 1×10^4 .

D. LEIGHTON

1164. The thermolysis of the rare-earth and other metal nitrates. W. W. Wendlandt (Texas Tech. Coll., Lubbock, Texas, U.S.A.). *Anal. Chim. Acta*, 1956, **15** (5), 435–439.—Thermolysis curves for the nitrates of the following metals show that decomp. to oxides is complete at the temp. indicated—La 780°, Ce^{III} 450°, Pr 505°, Nd 830°, Sm 750°, Sc 510°, Y 480°, U 550°, Th 480°, Zr 575°. Oxy-nitrates of the general formula MON_3 are shown to be intermediate products in the decomp. of the nitrates of La, Pr, Nd, Sm and Y.

W. C. JOHNSON

1165. Precipitation of actinium oxalate from homogenous solution. M. L. Salutsky and H. W. Kirby (Mound Lab., Miamisburg, Ohio, U.S.A.).

2.—INORGANIC ANALYSIS

Anal. Chem., 1956, **28** (11), 1780-1782.—After ion-exchange separation, Ac is pptd. free from inactive ions as follows. The soln. is evaporated and adjusted to a pH of 1 to 2 with HNO_3 and aq. NH_3 and the concn. to 7 mg of Ac^{3+} per ml. This soln. is digested at 60° to 70° with dimethyl oxalate and the Ac oxalate pptd. is filtered off, dissolved, and re-pptd. The second ppt. is decomposed with HNO_3 and the residue ignited to Ac_2O_3 and weighed. A 97% recovery of Ac is obtained. Solubility data for Ac and La oxalates are presented.

D. A. PANTONY

1166. Spectrum excitation by a powerful impulse spark in the analysis of tin bronzes. A. S. Alek-sandrova and S. P. Davydov. *Tekhnol. Trans. Mashinostroenie*, 1955, (4), 51-53; *Ref. Zhur. Khim.*, 1956, Abstr. No. 25, 982.—The analysis of tin bronzes for Zn, Pb, Sn, Ni and Fe is carried out by using a low-tension generator of powerful impulse discharges (illustrated). The sample is cast in a metal mould and cut in two pieces. Before the analysis, the surface of the block is covered with a thin layer of an insulating paste (rosin - ozokerite-bitumen - petroleum jelly) (35:50:7:8), and the block is glued to a plastics washer of diam. 15 mm and thickness 1 mm, with four equally spaced holes of diam. 1.2 mm. A special press fitted with points firmly presses the washer to the sample and pierces the layer of paste, thus removing the insulation in four places. The spectra are photographed three times on the spectrograph ISP-22, with slit width 0.03 mm, with a spherical condenser. A pointed carbon electrode is used as the positive pole, the sample as the negative; the distance between the electrodes is 1.5 mm. The lines used for the analysis are—Sn 2840·0 and Cu 2824·4; Pb 2833·0 and Cu 2824·4; Fe 2755·7 and Cu 2824·4; Zn 2502·0 and Cu 2529·4; Ni 3050·8 and Cu 3063·4 A. The analysis of the five elements may be carried out on one spectrum. During work on the method with three standards the mean square error was $\text{Pb} \pm 5.2\%$, $\text{Sn} \pm 4.0\%$ and $\text{Zn} \pm 5.4\%$.

C. D. KOPKIN

1167. Detection of lead in ores by the method of grinding. E. P. Ozhigov, M. A. Rafienko and L. K. Ivanenko (V. L. Komarov Far Eastern Filial, Acad. Sci., U.S.S.R.). *Zhur. Anal. Khim.*, 1956, **11** (3), 361-362.—Small amounts of Pb ($< 0.0002\%$) in various ores can be detected by grinding the material first with KHSO_4 and then with KI and heating the reaction mixture if necessary. Lead gives an orange colour.

G. S. SMITH

1168. Polarographic determination of lead and cadmium in zinc-base alloys using electrolytic separations at controlled potential. J. K. Taylor and S. W. Smith. *J. Res. Natl. Bur. Stand.*, 1956, **56** (5), 301-303.—A solution of the sample in HCl is electrolysed with a mercury-pool cathode, at a controlled potential of 0.9 V (vs. the S.C.E.). The residual solution is replaced by fresh electrolyte and the potential adjusted to 0.35 V, with the effect of anodically dissolving the Pb and Cd from the mercury-pool electrode. The separated metals are then determined by normal polarographic methods. Hydrazine dihydrochloride (≈ 0.1 g) is used as an anodic depolariser.

S.C.I. ABSTR.

1169. Determination of lead sulphate by means of cation exchangers. G. Gabrielson (A. B. Tudor, Nol, Sweden). *Anal. Chim. Acta*, 1956, **15** (5), 426-428.—The method is applied particularly to the determination of the degree of sulphation of

storage battery plates. *Procedure*—Boil a sample (≈ 6 g) from the plate for 1 hr. with a soln. of 0.5 g of Na_2CO_3 in 200 ml of water. Cool, saturate the soln. with CO_2 , filter off the PbCO_3 and wash with water saturated with CO_2 . Boil the filtrate with cation exchanger Amberlite IR-120 to decompose the excess of Na_2CO_3 , and complete the removal of the cations by passing the soln. through a layer, 20 to 30 mm deep and 10 mm in diam., of the same exchange material. Wash the column with 50 ml of water, boil the combined eluates to remove CO_2 , cool, and titrate the H_2SO_4 with 0.1 N NaOH.

W. C. JOHNSON

1170. Estimation of traces of zirconium in rocks, minerals and water. H. Degenhardt (Mineral.-Petrograph. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **153** (5), 327-335.—The rocks and minerals are decomposed by fusion with a mixture of NaOH and Na_2O_2 . Zirconium is separated by treatment with aq. NH_3 ; Fe^{III} present is reduced to Fe^{II} and Zr is determined colorimetrically with alizarin red S. As little as $2 \times 10^{-4}\%$ of Zr may be determined.

M. F. C. LADD

1171. Thorium complex of 1:8-dihydroxy-2:7-dinitrosonaphthalene-3:6-disulphonic acid. I. Detection and volumetric determination of thorium. Sachindra Kumar Datta (Darjeeling Gov. Coll., India). *Anal. Chim. Acta*, 1956, **15** (5), 415-420.—An acid soln. of 1:8-dihydroxy-2:7-dinitrosonaphthalene-3:6-disulphonic acid (**I**) changes from red to pinkish violet on the addition of Th^{4+} . From conc. soln. a ppt. is obtained which contains the reactants in the ratio 2Th:**3I**. Quantities of Th down to 1 μg can be detected in one drop of soln. at pH 4 by adding a drop of a 0.05% aq. soln. of **I** and comparing the colour with that of a blank. On filter-paper the limiting sensitivity is 2.5 μg ; a drop of the reagent soln. is applied first and partially dried, a drop of the test soln. is applied to the spot, which is again partially dried. **I** can also be used as an indicator in the titration of Th^{4+} with oxalate. *Procedure*—Adjust an aliquot of the test soln. to a pH of 3.0 to 3.8, add 2 ml of a 0.05% soln. of **I**, dilute to 50 ml, heat to 60° and titrate with 0.02 M oxalic acid until the colour changes from pinkish violet to red. Errors in the range -0.33 mg to +0.06 mg are recorded for the titration of 4.85 mg of Th. Interference is caused by Hg^{II} , Sn^{II} , Pb, Cu, Fe^{III} and Zr.

II. Spectrophotometric determination of thorium. Sachindra Kumar Datta. *Ibid.*, 1956, **15** (5), 421-425.—Factors affecting the formation and measurement of the colour of the Th-**I** complex are investigated and the following spectrophotometric method is presented. *Procedure*—To an aliquot of soln., containing up to 100 μg of Th^{4+} , add a 0.05% soln. of **I** (approximately 1.5 ml per 77 μg of Th present), dilute to nearly 25 ml, adjust to pH 2.5 with 0.1 N HCl and dilute to 25 ml. Determine the extinction at 370 $\text{m}\mu$ in comparison with a reagent blank. The following ions interfere in greater or less degree— Ca^{2+} , Ba^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} , Zr^{4+} , Ce^{4+} , PO_4^{3-} , F^- , CN^- and citrate.

W. C. JOHNSON

1172. *p*-Phenylenediamine derivatives as reagents for ultra-violet absorptiometric determination of nitrite ion. D. F. Kuemmel and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1674-1678.—Nine *p*-phenylenediamine derivatives, especially chloro-*p*-phenylenediamine, are examined as reagents for spectrophotometric determination of NO_2^- . Extinction coeff.

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D. A. PANTONY

1173. New gravimetric method for determining the nitrite ion by means of nitriton B (o-benzenesulphonamidoaniline). N. P. Komar' and I. U. Marshyñchenko (A. M. Gor'ki' Kharkov State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (3), 259–263.—Nitrites are quantitatively pptd. in soln. of pH 1.5 to 2.8 by nitriton B (2.48 g of the reagent in 1 litre of 0.2 M H₂SO₄), with 1.5 g-mol. of nitriton B to 1 g-ion of NO₂⁻. The ppt. is 1-benzenesulphonylbenzotriazole. Its solubility in water is $\approx 3 \times 10^{-4}$ M. To determine NO₂⁻, the test soln. is mixed with the reagent soln. and *M* Na₂CO₃ is added to give a pH of 1.5 to 2.8. The soln. (75 ml) is set aside in the dark for 8 hr., the ppt. is then collected on a glass filtering crucible and washed, first with 0.1 M H₂SO₄ and then with water, and dried in a stream of dry air at 75° for 20 min. Oxidising agents interfere, but the only other ions pptd. are Ag⁺, Hg₂²⁺ and Hg²⁺. G. S. SMITH

1174. Radiochemical determination of phosphorus-32. W. B. Silker (Hanford Atomic Products Operation, Gen. Elect. Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1782–1783.—The separation and determination of ³²P from a variety of radionuclides are described. A reproducible yield of 86.6% was obtained as molybdochosphoric acid after sorption of ⁷⁶As on a bed of CuS, and extraction from H₂SO₄ (1.3 N), which dissolves ³¹Si, by means of a 10% solution of *n*-butanol in diethyl ether. E. G. CUMMINS

1175. The rapid determination of phosphates in steam. M. V. Parshtutina. *Naladochnyye i Eksperiment. Raboty ORGRES*, 1955, **11**, 34–36; *Ref. Zhur., Khim.*, 1956, Abstr. No. 32,787.—Phosphates are determined by the intensity of the blue colour of the molybdochophosphate complex, extracted from water by *n*-butanol or isoamyl alcohol. The sensitivity of the method corresponds to 0.02 mg of PO₄³⁻ per litre. The presence of silicon compounds does not cause interference. The acidity must be 0.5 N in HCl. C. D. KOPKIN

1176. The determination of phosphates in boiler water. M. V. Gapchenko. *Nauch. Trudy Odess. Výssh. Morekhod. Uch.*, 1955, **1**, 150–153; *Ref. Zhur., Khim.*, 1956, Abstract No. 32,788.—In the determination of P₂O₅ by the molybdate-tin method, it is recommended that, for the preparation of a series of standards, a solid colloidal soln. of Fe₆[Fe(CN)₆]₃ in a dry gelatin layer of a photographic plate be used, as this completely replaces the natural series and lasts for a long time. The plates are treated in red light with a 20% soln. of Na₂S₂O₃ containing NH₄Cl until all the AgBr is removed, then washed, placed for 5, 10, 15, 20 and 25 min. in a 2% soln. of FeCl₃·6H₂O, and finally washed three times by decantation with water. The plates are then treated for 10 to 15 min. with a 2% soln. of K₄Fe(CN)₆ until no further increase in colour takes place, washed and dried. The plates must be standardised against a natural series of standards. C. D. KOPKIN

1177. The determination of the phosphoric oxide content of polyvanadates. V. Fleps and J. Inczédy (Dept. General Chemistry, Tech. Univ., Budapest). *Magyar Kém. Foly.*, 1956, **62** (9), 322–325.—A method for the quant. determination of a little P₂O₅ in the presence of much V₂O₅ is described. The vanadate is dissolved in a mixture of conc. H₂SO₄ and conc. HCl. The soln. is treated with a reducing agent to reduce VV and is transferred to an acidic ion-exchange column. In the vanadium-free soln., P₂O₅ is determined photometrically with ammonium molybdate and ascorbic acid.

A. G. PETO

1178. Absorptiometric determination of arsenic in minerals by hypophosphite. D. P. Shcherbov and K. I. Don. Report on Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 160–166; *Ref. Zhur. Khim.*, 1956, Abstr. No. 39,838.—The sample of ore with 1 ml of a mixture of HNO₃ and HCl (1:1) is heated to disintegration and evaporated to dryness. The residue is moistened with HCl, 10 ml of H₂SO₄ is added and evaporated until SO₃ vapours are evolved; after cooling, water is added and the evaporation is repeated. The residue is cooled, dissolved in 40 to 50 ml of water and aq. NH₃ is added until a slight odour of NH₃ is observed. The ppt. of Al₂O₃ is filtered off and washed with hot water containing aq. NH₃, then dissolved in 1 to 2 ml of dil. HCl (1:1), filtered and the residue washed with a small volume of HCl (1:1); the total volume of filtrate should be < 5 ml and to it is added 1 ml of 1% CuSO₄ in HCl (1:1), 1 ml of gelatin soln., 2.5 ml of 40% hypophosphite in HCl (1:1) and dil. HCl (1:1) to 10 ml. The soln. is mixed and heated on the steam bath for 10 min., then cooled, and the absorption is measured, with a blue or orange filter. A mixture of the reagents is used for comparison. The influence of Mo and Cu is removed by the use of an orange or yellow filter, and in the presence of V or Ni the measurement is conducted in the green part of the spectrum. For the determination of As in the presence of H₂SiO₃ it is necessary that the content of Fe in the solution amounts to about 30 mg. The most precise results are obtained with a content of As in the ore of 0.02 to 0.5%.

G. BREWER

1179. The volumetric determination of arsenate ions. E. Bakács and L. Szekeres (Univ. Agric. Sci., Budapest, Hungary). *Magyar Kém. Foly.*, 1956, **62** (9), 296–298.—Dissolve the sample, containing 0.05 to 0.1 g of AsO₄³⁻, in H₂O (3 to 5 ml). Add 1 to 2 ml of a buffer (50 g of NH₄Cl and 400 ml of conc. aq. NH₃, diluted to 1 litre with H₂O) to bring the pH to 10, followed by 96% ethanol (3 to 5 ml) (to obtain a 40 to 45% alcoholic soln.) and about ten drops of Eriochrome black T indicator (0.03 g in 20 ml of 96% ethanol) to obtain a medium-blue colour. Titrate with 0.1 M MgSO₄, with constant shaking. The first 1 to 3 ml (i.e., 20 to 25% of the expected titre) is added at once and the flask is shaken till the MgNH₄AsO₄·6H₂O crystallises out. The rest of the titration is carried out with the speed usual for pptn. methods. The colour change is blue to reddish violet (due to the formation of a complex between Mg²⁺ and the indicator), but in the presence of CrO₄²⁻ or Cr₂O₇²⁻ it is grey to pink. The indicator soln. is stable for about 15 days. Only PO₄³⁻ interfere. A. G. PETO

1180. Colorimetric determination of small quantities of vanadium in materials of high chromium content. Y. V. Morachevskii and M. N. Gordeeva.

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Vestnik Leningrad. Univ., 1955, (11), 139-148; *Ref. Zhur., Khim.*, 1956, Abstr. No. 43,498.—To determine V when Cr is present, a weighed sample is fused in an iron crucible with Na_2O_2 or in a platinum crucible with Na_2CO_3 and KNO_3 . The cooled, fused sample is lixiviated with water, filtered, and the residue washed. The aq. extract is acidified with H_2SO_4 , 5 ml of aq. H_3PO_4 (1:2) is added and H_2O to 100 ml. The mixture is boiled, 2.5 ml of 0.5 M Na_2WO_4 is added, and 20 ml of 40% aq. $(\text{NH}_4)_2\text{SO}_4$ soln. The ppt., after being heated for 2 to 3 hr., is filtered off, dissolved in 5 ml of 5% NaOH soln., diluted and boiled to remove NH_3 . The cooled soln. is neutralised with aq. H_2SO_4 (1:2), a small excess of acid is added and the colour is then measured. When Fe is present, the sample is dissolved and Fe^{2+} are oxidised to Fe^{3+} by the addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and ppted as Fe(OH)_3 ; the ppt. is filtered off and washed, and fused as described above.

R. LORD

1181. Quantitative inorganic chromatography. II. The determination of vanadium in the presence of excess of dichromate. F. H. Pollard, G. Nickless and A. J. Banister (The University, Bristol, England). *Analyst*, 1956, **81**, 577-581.—The difficulty of determining V in the presence of excess of dichromate is overcome by downward paper-chromatographic separation. The soln. is applied to a paper strip slotted to divide it into twin strips joined above the starting line. Identical vol. of soln. are applied to the strips and after the separation one strip is sprayed with tannic acid soln. and serves as a pilot strip to locate the V on the other. The solvent mixture used for equilibration and elution consists of water (15 ml), conc. HCl (4 ml), ether (50 ml) and methanol (30 ml). Some of the dichromate is reduced by the paper to Cr^{2+} and moves with the V, but the amount is insufficient to interfere with the subsequent colorimetric analytical methods described. A new chromatographic spraying reagent, Na 2-nitroso-1-naphthol-4-sulphonate, is described for the detection of dichromate. It is applicable also to the detection of Cu^{II} , Au^{III} , U^{IV} , Fe^{III} , Fe^{II} , Co^{II} , Ni^{II} , Pd^{II} and Pt^{IV} . Two spectrophotometric methods for the determination of V are described, the reagents being sodium tungstate and formaldoxime, respectively. As little as 20 μg of V in the presence of a 100-fold excess of Cr as $\text{Cr}_2\text{O}_7^{2-}$ can be determined with an error of $\approx +2\%$.

A. O. JONES

1182. The colorimetric determination of traces of vanadium in graphite anodes. L. M. Kul'berg and A. G. Shilova. *Uch. Zap. Saratov. Univ.*, 1955, **42**, 71-78; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,171.—The conditions for the method proposed by Alimarin (*Zhur. Prikl. Khim.*, 1944, **17**, 88) for the microcolorimetric determination of V in minerals are refined. It is found that the concn. of H_3PO_4 must be 6 to 7 N, and the quantity of benzidine and the temp. (0° to 20°) must be const.; in mixing the soln. it is recommended that the V be added last. The colour develops completely in 7 to 10 min., and after 30 min. its intensity begins slowly to fade. In ashing the sample without loss, first treat the finely ground carbon with 0.1 N NaOH , dry and ash in a muffle-furnace at 600° to 650° for 2 to 3 hr., or at 570° to 630° for 3 to 3.5 hr. Then extract V with H_3PO_4 (sp.gr. 1.7) and water, add benzidine and measure the extinction against water as a blank, with a cell depth of 20 mm and filter S42. The content of V is read off from a calibration curve.

C. D. KOPKIN

1183. Application of electrolytic methods of reduction in analytical chemistry. XI. Qualitative reaction for vanadium and molybdenum. G. T. Gal'yan and M. A. Indzhikyan. *Izv. Akad. Nauk ArmSSR, Ser. Fiz.-Matem., Estestv. i Tekhn. N.*, 1955, **8** (5), 51-54; *Ref. Zhur., Khim.*, 1956, Abstr. No. 39,845.—A soln. (3 ml) of $(\text{NH}_4)_2\text{MoO}_4$ or NH_4VO_3 in 10% H_2SO_4 is placed in an electro-reduction tube (diam. 2 cm, length 8 to 10 cm, closed with a collodion film at one end). A platinum cathode is immersed in the soln. and a current passed (5 to 6 V for the detection of Mo, and 3 to 4 V for the detection of V). In the presence of Mo the soln. acquires a yellow colour which changes to orange-red. In the presence of Cu, Ag or Sn, the soln. remains green; Fe and Mn do not interfere. In the presence of V the solution is coloured sky-blue. The sensitivity of the reaction for Mo is 0.0001 g in 3 ml, for V, 0.0003 g in 3 ml. In the presence of both V and Mo the soln. of these elements is reduced electrolytically in 10% H_2SO_4 by a current at 5 to 6 V. The colour of the solution changes from sky-blue (V) to yellow (Mo); Ti and W interfere. When Mo, V and Mn are present together, the Mn is detected by a current at 5 to 6 V in the anolyte.

G. BREWER

1184. Extraction separation of niobium, tantalum and titanium. F. V. Zaikovskii (All-Union Inst. of Mineral Raw Materials). *Zhur. Anal. Khim.*, 1956, **11** (3), 269-277.—At pH 3, *n*-butanol extracts Ti and Ta from soln. of their complexes with catechol and oxalate, leaving Nb in the aq. phase; Ti is separated from the extract by extraction with 5% H_2SO_4 . To separate a mixture of Nb_2O_5 , Ta_2O_5 and TiO_2 , the oxides (20 to 22 mg) are fused with 1 g of $\text{K}_2\text{S}_2\text{O}_7$, the cooled melt is dissolved in 25 to 50 ml of 3% ammonium oxalate soln., and the soln. is treated dropwise with Na_2SO_3 or dil. H_2SO_4 to give a pH of 3 to Tropaeolin OO indicator, followed by catechol to give a concn. of 20%. The soln. is repeatedly extracted with half its vol. of *n*-butanol, additional catechol being added each time. After four or five extractions, or when the soln. is nearly colourless (an indication of the complete removal of Ti), the final extraction is made without addition of catechol. The combined extracts are extracted several times with 5% H_2SO_4 or HCl. The *n*-butanol phase (mainly Ta) is evaporated, the residue is treated with 15 to 20 ml of water, and the soln. is again evaporated. The residue is dissolved in 20 to 25 ml of 8 to 10% H_2SO_4 , the cooled soln. is mixed with 8 to 10 ml of 3% cupferron soln., the ppt. is collected, ignited, and fused with the min. amount of $\text{K}_2\text{S}_2\text{O}_7$. The cooled melt is dissolved in 20 ml of 3% ammonium oxalate soln., catechol to give a concn. of 5% is added, the pH is adjusted to between 7 and 8 by addition of Na_2SO_3 , and the soln. is extracted with 8 to 10 ml of *n*-butanol. The extract is treated two or three times with 5% H_2SO_4 and the Ta is recovered by evaporating the *n*-butanol soln.; Nb and Ta are determined colorimetrically or gravimetrically. The phase separation of Nb, Ta and Ti is not affected by the presence of other elements.

G. S. SMITH

1185. An absorbent for oxygen in gas-analysis apparatus. M. N. Yashina. *Nauch. Trudy Odess. Morekhod. Uch.*, 1955, (1), 154-157; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,182.—The use of a soln. of CrCl_2 is recommended as an alternative to pyrogallol in the determination of O in gases. To obtain the CrCl_2 soln., first prepare an HCl soln. of CrCl_3 , and add aq. NH_3 . Wash the resulting

$\text{Cr}(\text{OH})_3$ ppt. with water till no more SO_4^{2-} appears in the filtrate, dissolve it in 200 ml of 2 N HCl and reduce Cr with zinc amalgam. To prepare the amalgam, add 5 g of granular Zn and a few ml of 2 N HCl to 100 g of Hg, and stir while warming on the water bath till the Zn has disappeared. Wash the cold amalgam by decantation with water, add the soln. of CrCl_3 and shake till the green colour changes to blue. Use the soln. of CrCl_3 so obtained to fill the absorption pipette of the gas-analysis apparatus to absorb O. One ml of a 20% soln. of CrCl_3 absorbs 9 ml of O. The soln. obtained is regenerated by shaking with zinc amalgam.

C. D. KOPKIN

1186. Determination of ozone by thermal conductivity. W. J. Burlant and W. A. Cannon (Chem. Dept., Sci. Lab., Ford Motor Co., Dearborn, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1801–1802.—Ozone is determined in ozonised oxygen over the range 0·5 to 1·6 mM by a normal thermal conductivity procedure, oxygen being used as reference gas. Results agree with those of the iodimetric procedure to within $\pm 2\%$.

D. A. PANTONY

1187. Remarks on the analysis of peroxy compounds and on the nature of the induction reactions involved. L. J. Csányi and F. Solymosi (Szeged Univ., Hungary). *Anal. Chim. Acta*, 1956, **15** (6), 501–505.—The analysis of mixtures containing H_2O_2 (**I**), peroxy sulphuric acid (H_2SO_5) (**II**) and peroxy disulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) (**III**) by the selective oxidation of H_2O_2 with KMnO_4 or $\text{Ce}(\text{SO}_4)_2$ is discussed in relation to the induction reactions involved and to the causes of error in the analyses. The simultaneous determination of **I**, **II** and **III** can be effected indirectly by reducing **II** with As_2O_3 and then titrating the H_2O_2 with $\text{Ce}(\text{SO}_4)_2$; **I** and **III** are then determined together in another sample in the presence of OsO_4 , **III** being titrated in the same sample after reduction with As_2O_3 . The analysis can also be made directly by first titrating **II** with As_2O_3 soln. (in the presence of KBr), then titrating the H_2O_2 formed (after addition of OsO_4) and finally titrating **III** while the soln. is warmed. The end-point is indicated by the dead-stop or the bimetallic method. Both the indirect cerimetric and direct As_2O_3 methods are applicable to the system $\text{H}_2\text{O}_2 - \text{H}_2\text{SO}_4$ and to mixtures of H_2O_2 with peroxyacetic acid or peroxyphosphoric acids.

W. J. BAKER

1188. Determination of small amounts of sulphur. F. Čúta, M. Hejtmánek and Z. Kučera (Inst. Anal. Chem., High School Chem. Technol., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (3), 370–372.—Small amounts of sulphur can be converted into H_2S when treated with Al in HCl; the H_2S is absorbed in a solution of a plumbous salt containing citrate buffer. The transmittancy of the resulting PbS (in colloidal form) can be measured photometrically. With this method, the content of S in thiourea, cystine, thiosulphate and allyl iso-thiocyanate, even in small amounts (3 µg), can be determined, with an error $> 7\%$, but it is not suitable for determining S in sulphite. J. ZÝKA

1189. Determination of traces of selenium. 3:3'-Diaminobenzidine as selenium(IV) organic reagent. K. L. Cheng (Materials Engng Dept., Westinghouse Elec. Corp., East Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1738–1742.—The production and spectrophotometric properties

of the yellow colour of the $\text{Se}^{\text{IV}} - 3:3'$ -diaminobenzidine complex are examined. The soln. containing $> 50 \mu\text{g}$ of Se is treated with formic acid, the pH is adjusted to between 2 and 3 and a dil. soln. of the reagent is added. After adjustment of the pH to between 6 and 7 with aq. NH_3 , the complex is extracted with toluene and the extinction is measured at 420 m μ vs. a reagent blank; the concn. of Se is derived from a calibration curve that follows the Beer-Lambert law up to 25 µg of Se. A standard deviation of $\pm 3.7\%$ is given. Oxidising agents, including Fe^{3+} , Cu^{2+} and VO_3^- , interfere, but the interference of the first two, and of most coloured ions, can be eliminated by addition of EDTA.

D. A. PANTONY

1190. The determination of selenium with ascorbic acid. F. V. Zaikovskii. Report of Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 142–146; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,362.—To determine Se volumetrically in technical selenium, add conc. HNO_3 (1 to 2 ml) to the sample (25 mg), and heat to between 70° and 80° on a water bath. After 20 to 30 min. dissolve the SeO_2 in 5 to 10 ml of water and dilute to 25 ml. To an aliquot add a known excess of freshly prepared ascorbic acid (**I**) soln. and 10 to 15 ml of 0·1 N HCl. A red colour is formed, followed by pptn. of Se. After 1·5 hr. titrate the excess of **I** with 0·01 N iodine in the presence of starch. To determine Se gravimetrically in artificial mixtures close in composition to Se-containing ores and minerals, treat 5 to 20 g of sample with HNO_3 in a porcelain crucible and heat on a water bath till moist salts are obtained. Add conc. HCl (20 to 30 ml) and 40% formaldehyde soln. (5 ml) and heat. Add 20 to 30 ml of water and filter by decantation. To the filtrate (40 to 60 ml), 3 N in HCl, add **I** (0·5 to 0·6 g) and after 1·5 to 2 hr. filter through a weighed crucible (No. 4 porosity). Wash the selenium ppt. with water and ether, dry at 100° to 110° for 10 to 15 min. and weigh. In the colorimetric determination, treat the washed selenium ppt. with conc. HCl (5 ml) and conc. HNO_3 (0·5 ml), warm for 5 to 6 min. on the water bath, and add 2 ml of formaldehyde soln. Add 15 to 20 ml of water, filter, add 5 to 10 ml of a 1% soln. of gelatin and 0·5 g of **I** to the filtrate. Stir for 40 to 50 min., dilute to 50 or 100 ml and after 30 min. measure the absorption, with a standard for comparison. The gravimetric and colorimetric determinations take 4 to 5 hr.

C. D. KOPKIN

1191. The entrapped impurities accompanying the precipitation of selenium with sulphur dioxide from hydrochloric acid solutions. H. Bode (Anorg.-chem. Inst. Tech. Hochschule, Hannover). *Z. anal. Chem.*, 1956, **153** (5), 335–352.—The following impurities were determined in selenium prepared by pptn. with SO_2 in 1 to 8 N HCl solution—Bi, Cu, Cd, Sb, Sn, Mo, Hg, Pb, Tl, Ru, Rh, Pd, Os, Ir and Pt. The pptn. were made both at room temperature and at 100° under pressure. The entrapping of the substances found is discussed.

M. F. C. LADD

1192. Application of thio salts in analysis. II. Estimations based on decomposition of thio salts. Part D. Estimation of selenium and tellurium in selenates and tellurates. G. B. S. Salaria (Univ. of Allahabad, India). *Anal. Chim. Acta*, 1956, **15** (6), 514–517.—The quant. pptn. of Se^{VI} or Te^{VI} as sulphides can be effected by the addition, to a soln. of selenate or tellurate, of a large excess of 2 N

aq. Na_2S soln., followed by decomposition of the thio salt by heating to 100° with an excess of conc. HCl. The ppt. is collected in a sintered-glass crucible (porosity 4), then washed free from Cl^- , dried for 1 hr. (at 95° for selenium sulphide and at 105° for tellurium sulphide) and weighed. When Hg is determined by the decomposition of its thio salt (*cf.* Taimni and Salaria, *Anal. Abstr.*, 1955, **2**, 3356), ammonium acetate in cold soln. can be used in place of HCl.

W. J. BAKER

1193. The spectrographic determination of small quantities of lead, tin, antimony and arsenic in chromium oxide. Yu. S. Glagolev. Report of Symposium: "Sovrem. Metody Anal. Metall.", M., Metallurgizdat, 1955, 89-95; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,327.—A method is described for the determination of 0.0002 to 0.03% of Pb, 0.0002 to 0.03% of Sn, 0.0004 to 0.03% of Sb and 0.0005 to 0.03% of As in Cr_2O_3 . The spectrum is excited by an a.c. arc. To increase the sensitivity, place the sample in a hemispherical cavity (diam. 4.5 mm) in both the upper and lower carbon electrodes, which are placed vertically with a gap of 1 mm. The arc is struck at a distance of 250 mm from the slit without an illuminating lens. Results are given of experiments with different rates of evaporation of the mixture in samples of different composition and with different excitation procedures. It is found that decrease in the impurity content results in a decrease in the time required for complete volatilisation, so that, to increase the sensitivity, the taking of photographs of the spectra from several pairs of electrodes on the same plate is recommended, with a decrease of each exposure time. The preparation of synthetic standards is described. The lines used are—Pb 2614-178 - Cr 2607-906; Sn 2429-495 - Cr 2426-6; Sb 2311-469 - Cr 2329-6; As 2349-84 - Cr 2339-7 Å. The analyses are carried out by the photometric interpolation method. The determination is reproducible with an average deviation of 10 to 12%.

C. D. KOPKIN

1194. Kinetic methods of quantitative analysis. III. Determination of small amounts of molybdenum. K. B. Yatsimirkii and L. P. Afanas'eva (Ivanovo Chem.-Technol. Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 319-322.—Small amounts of Mo as molybdate can be determined from their accelerating action on the reaction between H_2O_2 and KI in the presence of acid. The rate of the reaction is found from measurements of extinction at $\approx 553 \text{ m}\mu$. The accuracy of the method is confirmed over the concn. range 1.8×10^{-7} to $9.1 \times 10^{-7} \text{ M}$.

G. S. SMITH

1195. Determination of molybdenum by the isotope dilution method. M. L. Geldhof, J. Eeckhout and P. Cornand (Lab. Anal. Scheikunde, Univ. Gent, Belgium). *Bull. Soc. Chim. Belg.*, 1956, **65** (7-8), 706-718.—This method has been examined with the use of ^{99}Mo as tracer. Reliable results have been obtained for 1 to 20 mg of Mo, by either beta or gamma counting. The method has been applied to the determination of Mo in steel; if Cu is present, a correction must be made for the copper content of the molybdenum ppt.

P. HAAS

1196. The separation of molybdenum and iron using ion-exchange chromatography. I. P. Alimirin and A. M. Medvedeva. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1955, **6**, 351-364; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,335.—The optimum conditions for the separation of Mo and Fe in

the presence of citrate ions by ion exchange on Wofatit R and SBS are studied. On passing citrate soln. of a molybdate containing HCl through the column, all the Mo ($\approx 1 \text{ mg}$) in 0.1 N HCl is found in the filtrate. Increasing the molybdenum content to about 100 mg and, in particular, raising the concn. of HCl (to 0.5 N) leads to partial adsorption of Mo. Increasing the concn. of citric acid (**I**) lowers the adsorption of Mo in all cases to nil (at **M I**). Iron from FeCl_3 (HCl concn. 0.01 to 0.1 M) is completely adsorbed on the resins in the absence of **I**. At a HCl concn. $> 0.2 \text{ M}$, Fe passes into the filtrate. In the presence of **M I** there is a max. in the adsorption curve. Raising the HCl concn. from 0.01 to 0.1 M increases the adsorption from 44 to 100%. Further increase of acidity leads to Fe passing through again. In the analysis of soln. 0.1 N in HCl and **M** in **I**, no Fe is found in the filtrate after passage through the column. To remove Mo from the column, from 150 ml (for 1 mg of Mo) to 250 ml (for 100 mg of Mo) of water is necessary. Separation is possible with Fe:Mo $> 3000:1$. The method may be applied to the analysis of samples of steel, iron ore and ferromolybdenum. In analysing steel, dissolve 0.1 g in HCl-HNO₃ and stabilise the pH with a citrate buffer soln.; Fe^{3+} are completely adsorbed at pH 1.0. If dissolved in HCl, the Fe as Fe^{2+} is completely adsorbed in the pH range 1.0 to 3.0. Regenerate the resin with 10% HCl. A method for the separation, on the same resins, of Fe and Mo, in the presence of H_2O_2 as complexing agent, is studied. Since H_2O_2 is largely decomposed in HCl soln. of Mo and Fe, sulphate soln. were used. The max. adsorption of Fe is observed at $\approx 0.1 \text{ N}$ H_2SO_4 , in which condition Mo is 99% adsorbed. Addition of H_2O_2 ensures the complete passage of Mo into the filtrate, by reason of the formation of a stable complex of Mo. The concn. of H_2O_2 needed is from 0.1 (for 1 mg of Mo) to 1% (for 100 mg of Mo). The removal of Mo from the column requires the same washing as in the first method. The anionic complex of Mo remains stable (in the presence of 1% H_2O_2) on increasing the H_2SO_4 concn. from 0.1 to 0.5 N. Delays of more than 30 min. from the addition of H_2O_2 to the passage through the column lead to loss of Mo. In both variations of the method, 10 g of resin with granular diameter 1 to 1.5 mm was used; the rate of passage through the column was 3 litres per min. with a vol. of 50 ml.

C. D. KOPKIN

1197. The determination of molybdenum in its binary alloys with uranium by high-precision spectrophotometry. A. Bacon and G. W. C. Milner (A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1956, **15** (6), 573-579.—A direct and rapid determination of Mo, e.g., in U-rich binary alloys, can be made by measuring the extinction at 368 $\text{m}\mu$ in 1-cm cells (slit width 0.5 mm) of the Mo- H_2O_2 complex in soln. of 1.5 M H_2SO_4 and 0.18 M H_2O_2 . The extinction between 360 and 380 $\text{m}\mu$ is about twice that at 400 to 410 $\text{m}\mu$ in strongly acid soln. The small interfering absorbancy from UO_2^{2+} is corrected. The error is within $\pm 1\%$ for alloys containing $> 2.5\%$ of Mo, but below this level the error from U is greater. Procedure—Dissolve the sample (1 g) in 20 ml of 50% (v/v) H_2SO_4 plus a few millilitres of HNO_3 , evaporate until fuming, cool, add 20 ml of H_2O_2 and re-fume. Cool, dilute to 50 ml at 23° and determine the U by differential spectrophotometric measurement against suitable standards (*cf.* *Anal. Abstr.*, 1956, **3**, 1000). Then dilute 5 ml of the same soln. with 50% (v/v) H_2SO_4

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(6 ml), and H_2O (≈ 30 ml); after keeping the temp. at 23° , add 1 ml of 100-vol. H_2O_2 and make the soln. up to 50 ml. Measure the extinction (as described above) differentially against suitable standards, with the soln.-reversing technique.

W. J. BAKER

1198. New reagents for tungsten. III. Practical mineral analysis with the proposed new reagents. J. Zato (Fac. of Sci., Salamanca, Spain). *Inf. Quim. Anal.*, 1956, **10** (5), 161–167.—The effect is studied of the presence of impurities on the accuracy of determination of W by the reagents proposed previously (*cf. Anal. Abstr.*, 1956, **3**, 3619). The presence of up to 10% of H_2SiO_4 by weight of $Na_2WO_4 \cdot 2H_2O$ caused only very small effects on the accuracy, as did the presence of up to 50% by weight of Na_2S and pptn. from a 10% solution of NaCl. Alkaline decomposition of the tungsten ore is recommended since heavy metals are made soluble, cassiterite and silica are not attacked, formation of soluble manganates and permanganates is avoided, and adulteration with low-quality ferrotungstates can be detected. The procedure for tungsten minerals is given and data obtained with various samples are tabulated. It is noted that 4:4'-diamino-3:3'-dimethyltriphenylmethane gives results within 0.1% of those given with cinchonine, whereas the differences with 4:4'-diaminotriphenylmethane are of the order of 0.2%.

D. LEIGHTON

1199. The colorimetric determination of tungsten [in steel] with methyl violet. A. F. Nemirovskaya and V. I. Petrashev. *Nauch. Trudy Novocherkas. Politekhn. Inst.*, 1955, **26**, 237–245; *Ref. Zhur. Khim.*, 1956, Abstr. No. 25,957.—The colorimetric method consists in making a visual comparison with two standards or with a special series of standards. Neutralise the soln. of steel in a tube to phenolphthalein with HCl and add water, to a definite vol. Then add 0.5 ml of 0.5 N HCl, followed, after 10 min., by 1.2 ml of a 0.1% soln. of methyl violet. Mix, and compare the colour with a series of standards. With this method it is possible to determine 1 to 36 μg of W per ml in 20 to 25 min. It is established that, of the other ions present, Mo^{6+} , P^{3+} , V^{5+} and SO_3^{2-} give the most interference.

C. D. KOPKIN

1200. Investigation of the decomposition of thi tungstates by differential thermal analysis. L. Sokol (Phys. Chem. Lab., Záluží v Krušných horách, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 711–715.—An automatic apparatus for differential thermal analysis is described. On the basis of experimental results, the course of thermal decomposition of ammonium tetrathiotungstate is discussed and the following scheme of the reaction is proposed— $(NH_4)_4WS_4 \rightarrow 2NH_3 + H_2S + WS_3$; $WS_3 \rightarrow WS_2 + S$. By using this method, mixtures of diethio- and tetrathio-tungstates can be determined with an accuracy within $\pm 5\%$.

J. ŽÝKA

1201. Fluorimetric determination of uranium. F. A. Centanni, A. M. Ross and M. A. DeSesa (Raw Materials Dev. Lab., Nat. Lead Co., Winchester, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1651–1657.—The uranium-bearing material is attacked by standard methods and the neutralised soln. is extracted with ethyl acetate. Of this extract, 0.1 ml, containing approx. 0.1 μg of U_3O_8 , is drained into a 0.4-g pellet composed of 2% of LiF and 98% of NaF, which is then dried and fused at

900° under standard conditions. After 15 min. the pellets are examined in a fluorimeter and the content of U is determined by comparison with standards, allowance being made for a blank. Details of construction, use and maintenance of ancillary equipment are given. Precision is claimed to be $\pm 0.7\%$, and a high speed of repetitive analysis is quoted.

D. A. PANTONY

1202. Physico-chemical methods of control of uranium production. A. P. Vinogradov. Report of Symposium: "Issledov. Obl. Geolog., Khim. Metallurg.", M., Izdat. Akad. Nauk, SSSR, 1955, 72–89; *Ref. Zhur. Khim.*, 1956, Abstr. No. 36,199.—A review is presented of the methods of determining U that are applicable to control of its production. Briefly described are spectral methods for the determination of impurities in U, the determination of small quantities of U in powders, ores and intermediate products, an isotope addition method for the spectral determination of U in ores and intermediate products, an X-ray-spectral method of determination of U and its impurities, and the polarographic determination of U.

C. D. KOPKIN

1203. Determination of micro amounts of boron in uranium metal and in uranyl chloride solutions. L. Silverman and K. Trego (Atomics International, Canoga Park, Calif., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (5), 439–445.—The method previously described (*Anal. Abstr.*, 1954, **1**, 39) is adapted to the determination of B in uranium in amounts down to 3 p.p.m. The soln. of UO_2^{2+} is made slightly acid with HCl and a suitable quantity of oxalic acid soln. is added; curcumin soln. is then added and the soln. is evaporated to dryness at 55°. The residue is dissolved in acetone and the intensity of the red colour is measured at 535 μm . The expt. conditions necessary to obtain a residue completely sol. in acetone are somewhat critical. The prep. of B-free UO_2^{2+} soln., for use in reference blanks and in the prep. of a standard curve, is described, and a method is given for the treatment of insol. borides.

W. C. JOHNSON

1204. Coulometric titration with hypohalogenites. A. Liberti and P. Lazzari (Centro di Studio Chimico Generale, Rome). *Ric. Sci.*, 1956, **26** (3), 825–832.—The halogen is generated externally by electrolysis of the halogenide at a suitable pH (1.3, 5.8 and 7.5 for Cl, Br and I, respectively) and passed into a buffer solution (0.6 M $NaHCO_3$ for Cl or Br, and 0.01 M NaOH for I) containing the substance to be oxidised. The end-point is determined amperometrically with a rotating platinum micro-electrode polarised at +0.2 V for OBr^- and OCl^- in the presence of Br^- , and at 0 V for O^- . With the first two compounds, arsenites, NH_3 , ammonium salts, thiocyanates, benzenesulphonates, Sb K tartrate, alanine and aminobutyric acid can be titrated to an accuracy of $\approx 1\%$. Hypoiodite is effective only with strong reducing agents, but can be used for the titration of alkali borohydrides.

L. A. O'NEILL

1205. Detection of fluorine in minerals and ores by the method of grinding. E. P. Ozhibgov (V. L. Komarov Far Eastern Filial, Acad. Sci., U.S.S.R.). *Zhur. Anal. Khim.*, 1956, **11** (3), 363–364.—To detect F, the material is ground with $KHSO_4$, a small amount of $FeCl_3$ and then two or three small crystals of $KSCN$ and Na_2SCN are added, followed by a small amount of water. The presence of F causes decolorisation of $Fe(SCN)_3$.

G. S. SMITH

1206. The mercurimetric determination of chlorides in nitrate baths, electroplating solutions and other materials. G. N. Chernukha and K. M. Churkina. Report of Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 220-222; *Ref. Zhur., Khim.*, 1956, Abstr. No. 25,996.—Dissolve KNO_3 (10 g) in water (50 ml), add 5 ml of HNO_3 (1:1) and 1 ml of a 10% soln. of sodium nitroprusside, and titrate with 0.1 N $\text{Hg}(\text{NO}_3)_2$ soln. to the appearance of a permanent turbidity. To determine Cl^- in dipping soln., dilute 1 to 2 ml, and titrate as above. To determine Cl^- in chromate replenishing baths, titrate 20 to 50 ml. To determine NaCl in a nickel electrolyte, remove Cu^{2+} , Co^{2+} and Ni^{2+} by passing the soln. through a column of cation-exchange resin SBS (N form); dilute 5 ml of electrolyte to 50 ml and pass through the column at 0.5 to 1.5 ml per min., and wash with water (150 to 200 ml). Determine Cl^- in the filtrate as described above. The method gives results as accurate as those of argentimetry.

C. D. KOPKIN

1207. Mercurimetric method of determining iodides. R. Kh. Zamanov (I. P. Pavlov Samarkand Med. Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 329-331.—The solution (1 ml) containing $\simeq 0.13$ to 0.15 g of I^- in 100 ml is mixed with 5 ml of 96% ethanol, two drops of 1% diphenylcarbazone soln. and one or two drops of HNO_3 , and titrated with 0.01 N $\text{Hg}(\text{NO}_3)_2$ to a pale violet-red coloration. The use of an aq. ethanol medium avoids the formation of a ppt. of HgI_2 , and the results are not subject to a correction.

G. S. SMITH

1208. Spectrophotometric determination of rhodium. V. W. Meloche and R. L. Martin (Dept. of Chem., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1671-1673.—A perrhenate soln. (6 to 7 ml containing 0.07 to 1.4 mg of (Re) is treated in 6 N HCl with dil. Cr^{2+} soln. under N. After making the hexachlororhenate^{IV} soln. up to a standard vol., the intensity is measured with respect to a blank containing Cr^{2+} , and compared with standards, at 281.5 μm . An average deviation of 0.34% is given. Reference is made to the removal of interferences.

D. A. PANTONY

1209. The separation of iron valencies by paper chromatography. H. M. Stevens (Long Ashton Res. Sta., Bristol Univ., England). *Anal. Chim. Acta*, 1956, **15** (6), 538-542.—The quant. separation of Fe^{2+} and Fe^{3+} in acetate buffer soln. (pH 4) by descending chromatography, with the solvent system *n*-butanol - ethanol - glacial acetic acid - water (8:5:5:7, by vol.) is described. The chromatogram is run for 2.5 to 3 hr. (Whatman No. 1 filter-paper pretreated with 2 N HCl), and the valency bands are revealed by exposure to steam containing oxine; R_F values are $\simeq 0.2$ to 0.3 for Fe^{2+} and 0.8 to 0.9 for Fe^{3+} . The concn. of Fe in each band is determined by ashing completely the cut strip with HNO_3 (25 ml) and HClO_4 (2 ml), converting the residue into $\text{Fe}(\text{SCN})_3$, which is then extracted into a mixture of *n*-pentanol and ether (10 + 4, by vol.) for the spectrophotometric determination. The accuracy is high for samples containing $\simeq 2.5$ mg of Fe per ml. The prep. and properties (including absorption spectrum in pyridine) of a ferrous-8-hydroxyquinoline complex, probably $\text{Fe}(\text{C}_8\text{H}_7\text{ON})_2 \cdot 2\text{H}_2\text{O}$, are also given. The chromatographic method is specially suitable for biological samples.

W. J. BAKER

1210. The detection of iron as tri-*n*-butylammonium ferric thiocyanate. M. Ziegler, O. Glemser and N. Petri (Inst. Inorg. Chem., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **153** (4), 241-246.—A sensitive method for the detection of Fe^{3+} is described; it is based on the formation of the red compound $[\text{NH}(\text{C}_4\text{H}_9)_3]_3\text{Fe}(\text{SCN})_6$, which is insoluble in water but readily soluble in organic solvents. To 0.5 to 0.8 ml of acidified soln. add a few milligrams of thiourea, followed by NH_4SCN soln. (10%) (0.2 ml) and tributylamine (0.05 ml). Extract with amyl acetate (0.05 ml). The sensitivity is 0.05 μg of Fe^{3+} , or 0.1 μg of Fe^{3+} in the presence of large amounts of Mg, Ca, Al, Zn (add an excess of thiocyanate), Cd, Ni, Mn, Cr, V (the blue colour of the vanadium complex is modified to violet in the presence of Fe), Mo (yellow modified by Fe to orange), and smaller, specified, amounts of W, Pb, Sn, Sb and Co. The interference of Cu is prevented by the addition of thiourea.

P. S. STROSS

1211. Colorimetric estimation of iron by diphenylthiocarboxylic acid. L. C. Malik and R. P. Singh (Chem. Dept., Univ. Delhi). *J. Indian Chem. Soc.*, 1956, **33** (5), 335-338.—Diphenylthiocarboxylic acid is used for the colorimetric estimation of Fe^{II} in a photo-electric colorimeter (Klett-Summerson). Ferric iron can be reduced with quinol, an excess of which does not interfere. The maximum absorption due to the coloured complex is in the region of 660 μm ; this remains unaltered by an excess of the reagent. The determination of Fe can be accurately carried out when the concentration is between 0.2 and 1.2 parts per million parts of solvent. The effect of various ions and other factors on the coloured complex is studied; Cl^- , Br^- , I^- , NO_3^- , NO_2^- , SO_4^{2-} and SCN^- do not interfere even if present in relatively large quantities (100 times the quantity of Fe). Oxalate, citrate and tartrate interfere if present even in small quantities. Alkali and alkaline-earth metals cause no interference even at high concentration (500 p.p.m. for 2 p.p.m. of Fe). Copper cannot be tolerated at all, Ag only up to 10 p.p.m., Au up to 20 p.p.m., Al up to 20 p.p.m., and Cr up to 40 p.p.m., and Ni, Zn, Pb, Hg, Sn^{4+} , Mn and Mg can be tolerated even up to concentrations 100 times that of the Fe.

I. JONES

1212. The simultaneous determination of iron and aluminium with aluminon. L. A. Molot and L. M. Kul'berg. *Uch. Zap. Saratov. Univ.*, 1955, **42**, 79-83; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,165.—The absorption spectra of the vivid lakes formed by Fe and Al with aluminon at pH 4.67 (acid phthalate buffer) are measured. It is recommended that the determination be carried out at 530 μm . Calibration curves have been constructed for the lakes of both elements, with acetate (pH 4.40) and acid phthalate (pH 4.67) buffer soln. It is shown that in both cases the curves are close together, and cross when using the acid phthalate buffer. The deduction has been made that the sum of Al and Fe may be determined from the curve for Al or from the straight line that crosses both curves, passing through the point corresponding to the measured extinction and parallel to the abscissa axis. The following method of analysis is proposed. Dilute the sample with buffer soln. to 5 ml, add 0.1 ml of a soln. of aluminon (5 mg per ml), and measure the extinction 5 or 10 min. after mixing the soln.; determine Fe in an aliquot of the soln. by the thiocyanate method. The method has been tested on artificial mixtures and used in the analysis of

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2.—INORGANIC ANALYSIS

[Abstr. 1213-1218]

water glass and silica gel; satisfactory results have been obtained.

C. D. KOPKIN

1213. Coulometric titration of iron, cerium and vanadium with titanous ion. J. J. Lingane and J. H. Kennedy (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (5), 465-472.—The current efficiency for the generation of Ti^{3+} at a platinum cathode in HCl and H_2SO_4 media has been evaluated as a function of generating current density, concn. of Ti^{4+} and acid concn. With 6 M to 8 M H_2SO_4 containing 0.6 M $TiOSO_4$, the generation of Ti^{3+} is 100% efficient up to a current density of 3 mA per sq. cm. With this medium, Fe^{3+} , Ce^{4+} , V^{5+} and V^{4+} can be titrated coulometrically with errors up to $\pm 0.3\%$.

W. C. JOHNSON

1214. Analytical applications of the sodium arsenite - ferricyanide reaction, catalysed by osmium tetroxide. F. Solyomosi (Inst. Inorg. and Anal. Chem. Sci. Univ., Szeged, Hungary). *Magyar Kém. Foly.*, 1956, **62** (9), 318-322.—The reaction between $Fe(CN)_6^{3-}$ and arsenite, when catalysed by OsO_4 , is sufficiently rapid to be used for the quant. determination of $Fe(CN)_6^{3-}$ in a weakly alkaline soln. *Procedure*.—Dilute a sample, containing $Fe(CN)_6^{3-}$, with 4 N NaOH (20 ml) and, if necessary, with water, to make a 2 to 3 N NaOH soln. Warm it to between 70° and 75°, remove it from the flame, add 0.01 N OsO_4 [0.255 g in 0.1 N H_2SO_4 (100 ml)] (two to three drops) and titrate with 0.1 N As_2O_3 . The end-point can be detected either potentiometrically or by the dead-stop end-point method. Throughout the titration the temp. must remain above 50°. The method is suitable for the determination of $Fe(CN)_6^{3-}$ in various ppt. and for the back-titration of excess of $Fe(CN)_6^{3-}$ when used as an oxidising agent. In the presence of Hg^{2+} , the concn. of alkali must be doubled and the titration carried out at 25° to 30°. The accuracy is within $\pm 0.2\%$.

A. G. PETO

1215. Spectrochemical analysis of fabricated steel with the rotating electrode. J. P. Pagliassotti [Res. Dept., Standard Oil Co. (Indiana), Whiting, Ind., U.S.A.]. *Anal. Chem.*, 1956, **28** (11), 1774-1776.—The sample is dissolved in acid and transferred to a dish in which revolves a graphite disc, dipping below the surface of the soln. This disc acts as one electrode (positive) *vs.* a normal graphite electrode in an otherwise typical spectrographic apparatus. Calibration curves are presented for the following elements at the following wavelengths—Cr (2677.2, 2822.4), Cu (3274.0), Mn (2933.1), Mo (3170.4), Ni (3414.8, 3012.0), Si (2881.6) and V (3184.0), all with reference to Fe (3205.4) as internal standard. The relative error is given as up to 4%. Details of the rotating disc electrode are provided.

D. A. PANTONY

1216. The spectrographic analysis of steels of type P9, P18 and E1347 with a low-voltage spark. G. V. Leshchev and S. A. Makarova. Report of Symposium: "Sovrem. Metody Anal. Metall., M. Metallurgizdat," 1955, 55-59; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,374.—A method is described for the determination of W, Cr, V, Mn and Mo in quickly rusting steels. The spectrum is excited by a low-voltage spark. To stabilise the discharge, a needle, which is joined to the clamp of the lower electrode, is fixed near the upper electrode. The fixed electrode is of copper. Results are calculated by means of a conversion factor, with control standards, and the following lines—W 2397.09 - Fe 2396.71; Cr 2792.16 - Fe 2793.89; V 3063.25 -

Fe 3063.25; Mn 2933.06 - Fe 2936.9; Mo 2816.15 - Fe 2724.89 Å. To facilitate the calculation of results, a table has been prepared for the direct conversion of the corrected differences in blackening of the lines to concn.

C. D. KOPKIN

1217. The spectrographic analysis of complex steels with an alternating current arc. V. T. Bogdanova and K. I. Taganov. Report of Symposium: "Sovrem. Metody Anal. Metall., M. Metallurgizdat," 1955, 51-54; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,375.—A method is described for the analysis of steels EZh 1 and EZh 2 for Cr, Ni, Mn and Si, and of steel EYa 1T for these elements and Ti. The samples, of diam. 35 mm and height 110 mm, are cast in a metal mould. A copper rod serves as upper electrode, sharpened to a truncated cone; the arc gap is 2 mm. It is observed that there is a difference in composition between the main mass of metal in the sample and the outer zone; the samples are therefore treated with emery to a depth of 2 to 3 mm. Results are calculated by means of a conversion factor. The results are averaged from five spectra. The calculation of the concn. is taken from previously prepared tables. The lines used are—for EYa 1T and EZh, Cr 2690.26 - Fe 2689.21; Mn 2939.30 - Fe 2941.34; Si 2516.12 - Fe 2518.10; for EYa 1T, Ni 3080.76 - Fe 3083.74; Ti 3088.03 - Fe 3083.74; for EZh, Ni 3492.96 - Fe 3495.29 Å. The relative probable errors of the determinations of the various elements are within 0.6 to 5%.

C. D. KOPKIN

1218. The photocalorimetric determination of copper in cast iron and alloy steels. A. D. Sapir. Report of Symposium: "Sovrem. Metody Anal. Metall., M. Metallurgizdat," 1955, 48-50; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,303.—Place the sample of alloy steel (3 g) in a 500-ml conical flask, add a spiral of thick Cu-free aluminium wire, add hot H_2SO_4 (1:10) (100 ml), close the flask with a cork with a valve, and warm. As solution takes place the Cu separates. Dissolve high-Cr steels in 60 ml of freshly prepared H_2SO_4 (1:2). After solution has taken place, add hot water (160 ml), place an aluminium spiral in the flask and boil for 15 min. After solution of the sample, quickly filter off the copper and the carbides of the alloying elements through a cotton-wool filter in a funnel with a glass tap. Pack the cotton wool tightly into the funnel and place on it a short aluminium spiral. Wash the ppt. with cold water, then add hot acid to the funnel containing the ppt. and allow it to remain there for 3 min. before letting the liquor flow into the flask in which solution of the sample took place. Wash the filter with hot water; the black coating of carbides does not interfere. Transfer the cooled soln. to a 200-ml flask, add conc. aq. NH_3 (60 ml), cool, and make up to the mark. Filter a portion of the soln. through dry paper and measure the light absorption on photocalorimeter FEK-M, with a red filter, in a cell of depth 50 mm. Prepare a blank by mixing HNO_3 (1:2) (25 ml), conc. aq. NH_3 (60 ml) and water (115 ml). Read off the copper content from a calibration curve, constructed from standard samples of alloyed steels. To determine Cu in cast iron, dissolve the sample (3 g) by warming with H_2SO_4 (1:5) (40 ml), add 20% $(NH_4)_2S_2O_8$ soln. (50 ml) and boil for 10 min. Add 30% H_2O_2 soln. (5 ml) and boil for a further 5 min. Cool the soln., transfer it to a 200-ml flask, add, with shaking, conc. aq. NH_3 (100 ml), cool once more, make up to the mark, filter a portion and measure the absorption.

C. D. KOPKIN

2.—INORGANIC ANALYSIS

1219. The electrometric determination of aluminium in steel. S. V. Temyanko and I. P. Khazova. Report of Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 28-30; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,319.—To determine total Al, dissolve the sample of steel (0.01 to 0.1 g) by warming with HCl and HNO₃ and separate Al with alkali. Treat the soln. of Al or an aliquot by Chirkov's method (*Zavod. Lab.*, 1948, **14**, 7, 783) and titrate potentiometrically with NaF soln. To determine the content of metallic Al in the steel, dissolve 2 to 5 g of sample by warming with dil. HCl (1:1 or 1:3). Filter off the insol. residue (containing Al₂O₃) and determine Al in the filtrate by potentiometric titration with NaF soln. No interference is caused by Si, Cr, Ni, Co, Ti, W, V, Zr, Nb, Zn or Cu.

C. D. KOPKIN

1220. The spectrographic determination of silicon and manganese in Bessemer-furnace cast iron and steel. N. N. Tsvetkova, L. M. Epel'man and V. I. Dashchenko. Report of Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 60-63; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,379.—A rapid photometric interpolation method is described, in which a condensed spark is used. The samples and standards are in the form of rods with flat ends. The standards are selected from prepared samples. In the analysis of cast iron, a copper rod is used as upper electrode, of diam. 6 mm, sharpened to a truncated cone. The line pairs used are—Si 2881·6 - Fe 2880·8; Mn 2939·3 - Fe 2926·6 Å. The mean arithmetical error for Si is 1.4%, and for Mn 1.2%. The upper electrode in the analysis of steel is a graphite rod sharpened to a cone (120°). The lines used are—Si 2516·1 - Fe 2518·1; Mn 2939·3 - Fe 2926·6 Å. The mean error is $\approx 2\%$.

C. D. KOPKIN

1221. The spectrographic analysis of ferrosilicon. N. V. Kuz'mishcheva. Report of Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 72-77; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,368.—The samples of limiting and foundry cast-iron are cast in cylinders of diam. 5.5 mm, length 70 mm. The casts are prepared in a solid mould, ensuring rapid setting of the sample and homogeneity, with a fine granular structure. The investigation was carried out on blast-furnace ferrosilicon with a content of Si of 9 to 22% and of Mn of 1 to 4%. The spectra are excited in the condensed spark. The upper electrode is a copper rod of diam. 8 mm, sharpened to a truncated cone of surface diam. 1.5 mm. The lines used are—Si 2881·59 - Fe 2858·34 Å, and Mn 2933·06 - Fe 2926·58 Å. The analysis is carried out by the photometric interpolation method. The mean arithmetical error in one determination is 2% for Si and 3.1% for Mn. The time for the analysis is 35 min.

C. D. KOPKIN

1222. The spectrographic determination of oxygen in metals. I. Plain carbon steels. V. A. Fassel and R. W. Tabeling (Inst. for Atomic Res., Depart. of Chem., Iowa State College, Ames, U.S.A.). *Spectrochim. Acta*, 1956, **8** (4-5), 201-217.—The problems encountered in applying conventional spectrographic techniques to the determination of O in metals are surveyed and techniques for surmounting some of the problems are presented. For the determination of O in the range of 20 to 2000 p.p.m. in plain carbon steels, a d.c. carbon-arc excitation method can be used. This is based on the liberation of the O as CO in an argon atm. which supports an arc discharge between the sample

supported in a carbon electrode and a counter electrode. The concn. of O is derived from intensity ratios of the line pair O 7771·93 - A 7891·07. The precision attainable is comparable with the values obtained by most vacuum-fusion methods. At concn. of O of 0.01 to 0.1%, the standard deviation is about $\pm 6\%$, and at 0.002 to 0.05% it is about $\pm 11\%$. With suitably designed excitation chambers and with photo-electric measurement of intensities, 80 samples per day can be analysed. Preliminary data indicate that the method should be applicable to most metals and might be applied to the determination of O in solid org. compounds.

K. A. PROCTOR

1223. The spectrographic analysis of chromium and silicon in ferrochrome. L. N. Topalov. Report of Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 64-71; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,161.—The spectra are excited in an a.c. arc and photographed on spectrograph ISP-22, with slit width 0.02 mm and a graphite counter-electrode. The sample is sharpened and polished on an emery wheel. The lines used (in Å) and limits of concn. (%) are—Cr 2513·62 - Fe 2512·36 (60 to 75); Si 2516·12 - Cr 2530·45 (0·1 to 0·6); Si 2435·16 - Cr 2408·75 (0·5 to 2·5); Si 2532·38 - Cr 2530·45 (2·0 to 5·0). Calibration curves for Cr are constructed on the co-ordinates $\Delta S_{Fe/Cr}$ and $\log C_{Fe/Cr}$; the calculation of the concn. of Cr is made from the formula Cr (%) = $(100 - a)/(1 + R)$, where R = Fe, %/Cr, %, and a = percentage of Si plus all other impurities in the alloy. The mean value of these impurities is accepted as 0·6%. The graph for Si is constructed on the co-ordinates $\Delta S_{Si/Cr}$ and $\log C$. To obtain reproducible results, careful polishing of the surface of the sample is necessary. The relative error in the determination by three-fold photography of the spectra is $\pm 3\cdot1\%$ for Si and $\pm 0\cdot6\%$ for Cr. The high accuracy of the determination of Cr, as a basic component of the alloy, is explained by the homological nature of the pairs of lines selected, and by the very steep calibration curve. The deviation of the value of ΔS from the average value does not exceed 0·012.

C. D. KOPKIN

1224. The spectrographic analysis of ferrochrome for carbon, phosphorus and silicon. A. B. Shaevich. Report of Symposium: "Sovrem. Metody Anal. Metall., M., Metallurgizdat," 1955, 78-82; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,367.—In connection with the issue of standard ferrochromes, a method is proposed for the spectrographic determination of C, P and Si. Carbon is determined by using a condensed spark, with aluminium electrodes and a spark gap of 2·5 mm. The lines used are—C 2296·9 - Cr 2295·6 Å. It is possible to determine from 0·02% of C. The mean square error for three-fold photography of the spectra is 3%. To determine P, the spectrum is excited by an a.c. arc at 15 amp., the counter electrode being graphite. The lines used are—P 2149·1 - Cr \approx 2140·4 Å. It is possible to determine from 0·02% of P, with a mean square error of $\approx 7\%$. The silicon spectrum is excited at 3 amp. with an iron counter-electrode, slit width 0·01 mm. With a silicon content $< 1\%$ the lines used are—Si 2506·9 - Fe 2507·9 Å; with a higher content, Si 2435·2 - Fe 2443·9 Å. The error is 3%. A medium quartz spectrograph is used.

C. D. KOPKIN

1225. The polarographic determination of cobalt in steel. R. Wyndaele and F. Verbeek (Lab. Anal. Chem., Univ. Gent, Belgium). *Bull. Soc. Chim.*

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Belg., 1956, **65** (7-8), 753-767.—Two methods have been examined. The first is based on the reduction of Co^{III} to Co^{II} after oxidation of the Co^{II} by PbO₂ in the presence of EDTA. Interfering elements are pptd. with pyridine. The second method is based on the reduction of Co^{II} to Co after the separation of Co^{II} from all interfering elements by extraction of the complex ion Co(SCN)₄²⁻ with hexanone-ether, followed by extraction of the alcoholic phase with aq. NH₃ and destruction of the thiocyanate by heating with conc. HNO₃. Iron and chromium are separated previously. Both methods give very satisfactory results.

P. HAAS

1226. Analytical study of nioxime (cyclohexanedione-dioxime). Polarographic determination of nickel. P.-E. Wenger, D. Monnier and W. Bachmann-Chapuis (The University, Geneva, Switzerland). *Anal. Chim. Acta*, 1956, **15** (5), 473-483.—The dissociation constants of nioxime have been determined by means of potentiometric titrations of its soln. with standard NaOH and of a soln. of its sodium salt with 0.1 M HCl. The values $pK_1 = 10.4 \pm 0.2$ and $pK_2 = 12.7 \pm 0.3$ are obtained. Nioxime gives rise to polarographic waves at three different potentials according to the pH of the medium. In acid soln. (pH 2 to 4) 8 electrons are involved in the reduction; this number is reduced in less acid soln. and becomes 4.3 at pH 12. Soln. of pH < 5 are shown to be unstable by changes in their polarographic characteristics with the passage of time. The solubility product of the Ni-nioxime complex is derived from the end-point conditions when a soln. of the complex in 0.1 M HCl is titrated with 0.1 M NaOH to the appearance of a ppt. This method gives a solubility product of $\approx 10^{-27}$, whereas a value of $\approx 10^{-30}$ is derived from the polarographic determination of nioxime in a soln. that has been saturated with the complex by treatment with an excess of the solid substance. When the nioxime content of a soln. is determined polarographically before and after the addition of Ni²⁺, the difference provides a determination of the Ni added. The precision of this determination is $\pm 2\%$ for a nickel concn. of 6 μg per ml.

W. C. JOHNSON

1227. Compleximetric titrations. (Chelatometry.) XVIII. Determination of nickel and copper in cobalt and its salts. F. Vydra and R. Příbík (Res. Inst., Pharm. and Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (4), 539-541.—After the separation of Co in the form of NH₄CoPO₄, Ni in the filtrate can be determined with EDTA (disodium salt) (**I**) and Cu with 1:2-diaminocyclohexanetetracetic acid (disodium salt) (Chenta reagent) (**II**). *Procedure*—Dissolve the cobalt salt in a minimum of H₂O and add 100 to 200 ml of pptg. reagent. If necessary, add a few ml of aq. NH₃ to dissolve the amorphous ppt. Boil for 10 min., set aside for 30 min. on a water bath, cool slowly, filter, and wash the ppt. with warm H₂O containing aq. NH₃ and hydroxylamine. The removal of Co can be made quant. by using a repeated pptn., but this is not necessary. To the filtrate add HCl to a pH of 5 to 6, an excess of standard **I**, then aq. NH₃ to a pH of 8 to 10, and titrate with MgSO₄ soln. (for Ni and traces of Co); add H₂O₂ and KCN and titrate again with MgSO₄ (for Ni). For determining Ni and Cu in cobalt salts, use the same procedure for the removal of Co; then add an excess of standard **II**, titrate with MgSO₄ (for Cu, Ni and traces of Co), add H₂O₂ and KCN and continue with the titration (for Cu); the difference between the titrations with

I and **II** corresponds to the content of Ni. *Preparation of the pptg. reagent*—Dissolve Na₂HPO₄ (30 g), NH₄Cl (38 g) and hydroxylamine hydrochloride (4 g) in H₂O (800 ml) and add conc. aq. NH₃ (250 ml).

J. ZÝKA

1228. An increase in the accuracy of the determination of nickel and cobalt in the complete spectral analysis of rocks. V. V. Khokhlov. *Zap. Leningr. Gorn. Inst.*, 1955, **30** (2), 178-191; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,341.—As a result of the different composition of samples and standards in the spectral analysis of rocks (*Ref. Zhur., Khim.*, 1955, Abstr. No. 3820) the error in the determination may be several hundred per cent. To increase the accuracy of the analysis for Ni and Co, several series of standards have been prepared, taking into account the type of rock containing these elements. A preliminary spectrum informs on the type of sample, and the corresponding series of standards is used. As a result of this, the error of the analysis is lowered to a few tenths per cent. The standards are prepared from natural samples analysed chemically.

C. D. KOPKIN

1229. Colorimetric determination in the ultraviolet region of the spectrum of traces of copper in metallic nickel and its compounds. K. P. Stolyarov and F. B. Agrest (A. A. Zhdanov Leningrad Order of Lenin State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (3), 286-291.—Traces of Cu in the presence of large amounts of Ni can be determined from the u.v. absorption at 365 to 380 μm of the ammonium complex of Cu⁺. To determine Cu (0.01 to 0.03%) in metallic Ni, the sample (150 to 250 mg) is dissolved in dil. HNO₃, H₂SO₄ is added and the soln. is evaporated to dryness. The residue is dissolved in water, the soln. is filtered, 2 ml of 1% ascorbic acid soln. and 2 ml of saturated KBr soln. are added, and the boiling soln. is treated with dil. aq. NH₃ (1 + 5) to precipitate hydroxides. The filtered soln., in a 50-ml calibrated flask, is mixed with 25 ml of aq. NH₃ (1 + 1), diluted to the mark and then set aside for 30 min. A comparison soln. containing the same amount of Ni as the sample is prepared similarly. The extinctions are measured and the content of Cu is calculated from a calibration curve. Without separations, Cu can be determined when the elements Cu, Ni, Co and Zn are present in the ratio 1:1500:30:75. By co-pptn. of part of the Ni with Fe(OH)₃, the ratio of Ni to Cu can be increased to 4000:1.

G. S. SMITH

1230. Analysis of nickel alloys for the manufacture of cathodes. III. The determination of aluminium. G. Eckert (Wernerwerk f. Bauelemente, Siemens und Halske A.-G., Munich, Germany). *Z. anal. chem.*, 1956, **153** (4), 261-267.—The colorimetric determination of small concn. of Al (0.1 to 0.002%) in nickel alloys by means of aluminon is described. Aluminium is freed from the large excess of Ni and other metals such as Co, Fe, Mn, V, Pb, Sn and Cu by extracting these metals with Na diethyldithiocarbamate in a non-polar chlorinated hydrocarbon solvent (CCl₄, dichloroethylene). Silicon and Mg do not interfere, but W, Ti and Cr must be substantially removed before the final colorimetric determination of Al with aluminon. The method is also suitable for determining Al in iron alloys. The standard deviation is $\pm 6\%$.

P. S. STROSS

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1231. Determination of ruthenium in dilute solution by isotopic dilution and spectrophotometry. M. A. El Guebely (Lab. Curie, Paris, France). *Anal. Chim. Acta*, 1956, **15** (6), 580-584.—Two radioactive procedures for the determination of Ru^{III} in soln. of concn. 10^{-2} to $10^{-3} N$ and a spectrophotometric method of determining concn. of 7.5×10^{-4} to $10^{-5} N$ are described. (i) An aliquot of the soln. (in H₂SO₄) containing added radioactive Ru of known activity is oxidised anodically (c.d. = 4 mA per sq. cm) in the apparatus shown. The RuO₄ is removed in a current of air and absorbed in conc. HCl at 0°. The activity of the Ru^{IV} soln. is then measured and the Ru is determined gravimetrically as RuO₂ or metallic Ru. Certain other metals can be present, or the Ru can be present initially in any other valency. (ii) An aliquot of the sample soln. (either Ru^{III} or Ru^{IV}) containing a known amount of radioactive Ru is electrolysed at 90° to 100° (0.5 to 2 mA per sq. cm) for a certain time, the two compartments being separated by an electrolytic siphon. The activities of the residual electrolyte and of the deposit of Ru are measured and the deposit is weighed. The mean error for methods (i) and (ii) is $\pm 5\%$ (in comparison with Ru^{III} soln. titrated directly with thiosulphate). (iii) The sample soln. of Ru^{III} in 4 N H₂SO₄ is oxidised with gaseous Cl for ≈ 10 min. The soln. is kept for 90 min., the excess of Cl is boiled off, and the acidity of the cold soln. is adjusted to 0.4 N. The Ru^{IV} is then reduced with solid KI and the extinction of the liberated I is measured immediately at 410 m μ . The concn. of Ru^{III} is obtained from a calibration curve. The reproducibility is within $\approx \pm 3\%$. (Cf. *J. Chim. Phys.*, 1954, **51**, 290; 1956, **53**, 742.) W. J. BAKER

1232. The detection of palladium with substituted acetylenes. M. Ziegler and O. Glemser (Inst. Inorg. Chem., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **153** (4), 246-248.—The detection of Pd by the formation of a yellow insoluble acetylide, which is extracted by organic solvents, is described. To a weakly acidic soln. add a 1% soln. of isopropyl-acetylene in methanol and extract with amyl acetate or CHCl₃; 0.5 μ g of Pd can be detected by the yellow colour, and Pt⁴⁺, Rh³⁺, Ir⁴⁺ and most ions of the transition metals do not interfere. Although Cu, Ag and Pb interfere, they can be oxidised and pptd., and the interference of Au is overcome by using CHCl₃ for the extraction. A table giving the sensitivity of the test in the presence of several metals is included. P. S. STROSS

1233. The semi-micro gravimetric determination of palladium with piapelenole [benzo-2:1:3-selenadiazole]. M. Ziegler and O. Glemser (Inst. Inorg. Chem., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **153** (5), 352-354.—Palladium is pptd. by a 1% solution of piapelenole in methanol and the ppt. is dried at 110°; 10 to 20 mg of PdCl₂ was determined with a mean error of $\pm 0.7\%$. The semi-micro determination is practicable also in the presence of 10 to 20 mg of Pt⁴⁺, Ni²⁺, Co²⁺ and Pb²⁺, when 20 mg of PdCl₂ can be determined with a mean error of $\pm 0.5\%$. M. F. C. LADD

1234. An absorptionometric determination of iridium. S. S. Berman and W. A. E. McBryde (Univ. of Toronto, Toronto, Ontario, Canada). *Analyst*, 1956, **81**, 566-570.—A reaction between SnCl₂ and iridium salts in a medium of HBr produces an intense yellow stable soln. suitable for spectrophotometric measurement. The reagent is a 25% soln.

of SnCl₂·2H₂O in bromine-free conc. HBr. Several factors that influence the intensity and stability of the colour are discussed. The sample soln. in a test-tube is placed in a boiling-water bath and after 10 min. the reagent is added. After 2 min. the tube is cooled quickly in running water, the liquid is suitably diluted and the extinction is measured at 402 m μ . With precise adherence to the directions given, the method is applicable to samples that have been fumed with H₂SO₄. Owing to interference from other metals of the platinum group, Ir must be isolated before application of the method. The tolerances of other ions likely to cause interference are given. The method is more sensitive than any hitherto published. A. O. JONES

1235. Potentiometric micro-titration of iridium with quinol and other reducing agents. A. Berka and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 829-831.—Solutions of quinol, *p*-cresol, *p*-phenylenediamine and *p*-aminophenol have been examined for use in the reductometric determination of quadrivalent iridium salts, and quinol soln. was found to be the most suitable for micro-titration. *Procedure*—The soln. containing 100 μ g to 20 mg of Ir (in the form of IrCl₆²⁻ or chloride) and 5 to 20 ml of 10% HCl or 5% H₂SO₄ is titrated with 0.01 M to 0.0001 M quinol, with potentiometric indication. No interference is caused by salts of Pt^{IV}, Rh^{III} or Pd^{II}, or by many common metals (e.g., Fe, Co, Ni, Cu, Mn, W and Ti); salts of Au^{III} interfere. The soln. of *p*-benzoquinone was also examined; by using it as a volumetric oxidising agent, the titration of Ti³⁺ and Sn²⁺ and thiosulphate can be carried out. The soln. of quinhydrone can be used for reductometric as well as for oxidimetric titrations. J. ZÝKA

1236. Polarographic and polarometric study of some noble metals. VII. Polarographic behaviour of platinum. P. Beran and J. Doležal (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (3), 349-359.—Platinum, in a mixture of ethylenediamine and thiocyanate as supporting electrolyte, yields a well-developed polarographic wave, suitable for analytical purposes. The characteristics of the wave are discussed, the corresponding complex [Pt(en)(SCN)₂] has been isolated in the pure form, and the velocity of the complex formation studied. The polarographic behaviour of common and other noble metals in the same medium was also studied and their half-wave potentials are given. Platinum can be determined in alloys [Pt-Rh (2:1) and Pt-Ir (1:2)] with satisfactory accuracy. *Procedure*—Dissolve the sample (50 mg) in aqua regia, evaporate twice with HCl, wash the residue with H₂O into a 25-ml volumetric flask, and make up to vol. Mix 1 ml of the solution with 0.5 M ethylenediamine (1 ml), 4 M KSCN (0.5 ml) and 1 M KNO₃ (1 ml) and make up to 10 ml with H₂O; set aside for 24 hr. and record the polarographic wave. J. ZÝKA

1237. The spectrographic analysis of slags from the basic open-hearth furnace. V. V. Nalimov, V. G. Pines and S. A. Genshaft. Report of Symposium: "Sovrem. Metody Anal. Metall." M., Metallurgizdat," 1955, 87-88; *Ref. Zhur. Khim.*, 1956, Abstr. No. 29,385.—To prepare soln. of samples and standards, mix 0.1 g of the powder with water (20 ml), boil, add a mixture of conc. acids (20 ml of HCl and 3 ml of HNO₃) and a soln. of Cu(NO₃)₂ containing 2.28% of Cu. Introduce the

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[Abstr. 1238-1243]

soln. into a condensed spark discharge by means of a capillary. The analysis is carried out by the photometric interpolation method, or by using a microphotometer and a const. curve. The line pairs used for the determination of MgO , CaO , FeO , SiO_2 and MnO are— Mg 2790·78 - Cu 2766·37; Ca 3179·33 - Cu 3194·09; Fe 2382·04 or 3020·64 - Cu 2400·11; Si 2881·57 - Cu 2882·93; Mn 2949·2 - Cu 2961·6 A. The limits of the determinable concn. are— MgO 37 to 38; CaO 7 to 25; FeO 3 to 37; SiO_2 11 to 45, and Mn 1·5 to 9%. The mean error, depending on the element, is 3 to 6%.

C. D. KOPKIN

1238. Theory of fireclay products. II. K. Konoicky. *Ber. dtsch. keram. Ges.*, 1956, **33**, 52-59.—The mullite content of a fired product was determined by separation of the crystals with HF. *Procedure*—The powdered sample (< 0·06 mm) (0·5 g) is treated with 10 ml of HF (40%) at 0° in a shallow dish. The residues after a 1-hr. and a 4 to 7-hr. treatment are weighed and the content of Al_2O_3 determined. The mullite content of the sample is—(residue after 1 hr.) \times (Al_2O_3 content of 1-hr. residue/ Al_2O_3 content of 4 to 7-hr. residue). The results agreed well with those by X-ray diffraction and by calculation from the ultimate chemical analysis. J. A. SUGDEN

See also Abstracts 1099, 1100, 1102, 1103, 1105, 1106, 1108, 1109, 1243, 1352, 1353, 1380, 1404.

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1239. A modified apparatus for the quantitative micro-determination of carbon and hydrogen in organic compounds. F. E. Charlton (Chem. Defence Exp. Estab., Porton, Wilts., England). *Analyst*, 1956, **81**, 582-587.—A modification of an existing combustion apparatus (Ingram, *Brit. Abstr. A II*, 1942, 338) is described and illustrated. This permits the satisfactory combustion of difficult substances, particularly those containing P-F linkages, more rapidly than is possible with the Pregel apparatus. The value of MnO_2 as an external absorbent for oxides of N, with a packed form of combustion tube and low rates of flow (10 ml per min.) is confirmed. High figures for H may occur owing to the presence of films of moisture on boats and sampling tubes. Methods of eliminating this source of error are described. A. O. JONES

1240. Determination of carbon and hydrogen in organic fluorine compounds. Micro-combustion method for gases, liquids and solids. R. N. McCoy and E. L. Bastin (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1776-1780.—The classical tube-filling for the determination of C and H leads to high values for C in compounds containing F, owing to absorption of SiF_4 from the glass on to the Ascarite absorbent. High values for H are also obtained since with very little H present the nearly dry gas tends to dehydrate the PbO_2 used. A filling has been developed which overcomes these difficulties. An apparatus is described for the combustion of solid, liquid or gaseous samples in a tube at 900° packed with a 225-mm centre section of wire-form CuO flanked on each side by 50 mm of 8 to 20-mesh MgO (prepared according to Throckmorton and Hutton, *Brit. Abstr. C*, 1953, 1009) and 30 mm of 20-mesh rolled silver-gauze. Outside the combustion tube are a

Dehydrite tube for water, a manganese dioxide tube for oxides of N, and an Ascarite tube for CO_2 . A gas burette and a micro-pressure vessel are described for gas sampling and introduction to the system. Details of the gas flow control system are given. It was found essential to have the section of MgO after the section of CuO in the tube as not all the F is converted into an absorbable form until it has passed the CuO . The MgO must also be heated to 900° to avoid retention of CO_2 . Analyses of a number of substances are given.

E. J. H. BIRCH

1241. Rapid methods of micro-elementary analysis. XII. Simultaneous determination of carbon, hydrogen, silicon and halogens. V. A. Klimova and E. G. Bereznitskaya. *Zhur. Anal. Khim.*, 1956, **11** (3), 292-298.—For organosilicon compounds in which the halogen is attached to C, the weighed sample is placed in a small quartz vessel followed by 100 to 200 mg of asbestos previously ignited to 1200°, and the whole is weighed. If the sample is volatile it is placed in a glass ampoule and the ampoule, open end down, is placed in a small beaker and the asbestos is introduced. The vessel is placed in a combustion tube connected to three absorbers. The first, of heat-resisting glass, contains Ag (for halogens) and is heated to 500° to 550°. The second and third are for absorbing water and CO_2 , respectively. If the substance contains N, a further absorber is placed between the second and third. After the combustion, the beaker and the three absorbers are weighed. The method is also suitable for many other compounds containing halogen attached to silicon, but some of them give SiC in place of SiO_2 . In such cases a catalyst (Cr_2O_3) is introduced with the asbestos and a drop of water, the weight of which is deducted from the total weight of water found.

G. S. SMITH

1242. Decomposition of organic fluorine compounds by Wickbold oxy-hydrogen flame combustion method. P. B. Sweetser (Chem. Dept., E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1766-1768.—Organic compounds of F are vaporised or partly burned and passed into an oxy-hydrogen flame burning in a water-jacketed quartz tube, where complete conversion into HF occurs. The HF formed is cooled and absorbed in 50 ml of 0·1 N NaOH. The resulting fluoride is titrated with $Th(NO_3)_4$ in chloroacetic acid buffer at pH 3·4, with alizarin red S as indicator. The end-point is finally determined, in the dark, by the appearance of a faint pink colour under u.v. light. The method is preferable to combustion in the Parr bomb as there are no extra salts present to interfere with the end-point. A consistently slightly low result is interpreted as being due to the presence of boron from the glass, but is sufficiently regular to be allowed for. Compounds from tetrafluoromethane to "Teflon" (polytetrafluoroethylene) are satisfactorily analysed and even sodium trifluoroacetate is accurately analysed if the residual NaF in the combustion boat is added to the absorption soln. for titration.

E. J. H. BIRCH

1243. Organic quantitative analysis. VII. Rapid colorimetric determination of small amounts of sulphur in organic and inorganic material. M. Večeřa and A. Spěvák (Res. Inst. Org. Synth., Pardubice-Rybítví, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 765-769.—When treated with metallic potassium in a sealed tube, the sulphur in the sample

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is converted into sulphide. From the acid solution, H_2S can be distilled off and determined photometrically, with *p*-amino-NN-dimethylaniline. The procedure is suitable for the determination of sulphur in inorganic and organic materials, in a concn. range of 0.005 to 8% of S. J. ZÝKA

1244. Application of lithium aluminium hydride to the determination of hydroxyl groups. G. A. Stenmark and F. T. Weiss (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1784-1787.—Active H can be determined, even in the presence of epoxy groups, by measuring the H evolved with $LiAlH_4$ in tetrahydrofuran soln. The connections to the mercury gas-burette (described) are made through 14-gauge stainless-steel hypodermic tubing to increase flexibility and cut down dead space. The $LiAlH_4$ is dissolved in tetrahydrofuran and, after the addition of some 4-phenylazodiphenylamine as an indicator for free reagent, the soln. is filtered into storage flasks under N. The evolution reaction is carried out in a special flask with a side-arm in which the reagent can be held apart from the soln. of the sample in tetrahydrofuran while the burette is adjusted to zero position, and can then be allowed to react without opening the apparatus. Corrections are made for the blank (1 to 5 ml.), water (determined by Fischer titration) and acidity. The method is tested with particular application to epoxy groups and epoxy resins. E. J. H. BIRCH

1245. Indirect volumetric determination of carbonyl groups. A. Berka and J. ZÝKA (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 831-833.—Aldehydes and ketones are treated with an excess of standard 2:4-dinitrophenylhydrazine (**I**) and, after removal of the resulting 2:4-dinitrophenylhydrazone, the excess of the volumetric reagent is determined with chloramine T in the presence of KBr. *Procedure*—Dissolve the sample (0.3 to 10 mg) in 96% ethanol, add 0.01 M **I** (5 to 10 ml) and set aside for 12 hr. Filter through a paper filter, wash the ppt. with 2 N HCl (20 ml), dilute the filtrate to 50 ml, add KBr (1 to 2 g) and titrate with 0.01 M to 0.001 M chloramine T, using potentiometric control. When titrating less than 1 mg of the sample, a positive error appears. Fourteen aldehydes and ketones were determined with this procedure. J. ZÝKA

1246. Micro-determination of the nitrile group in acylated nitriles of the aldonic acids. B. Berinzaghi (Fac. Exact, Phys. and Nat. Sci., Buenos Aires). *An. Asoc. Quím. Argentina*, 1956, **44**, 120-121.—The Wohl nitrile degradation reaction is applied to the nitrile group of acetyl-, propionyl- and benzoylnitriles of arabinic, rhamnosehexonic, gluconic, galactoheptonic and galactonic acids, and to mannoheptonic nitrile. The sample (15 to 25 mg) in 2 ml of ethanol is treated with 50 mg of $AgNO_3$ and 2 ml of conc. aq. NH_3 . After being set aside for 24 hr. at room temp., the soln. is acidified with dil. HNO_3 (1:1), and the resulting $AgCN$ ppt. is filtered off, washed with ethanol and dried at 90° to 100°. The average error varied between 3.56 and 8.2%. D. LEIGHTON

1247. The determination of small quantities of water in films and organic liquids. K. Hoffmann and L. Fischer (Farbwerke Hoechst A.-G., Frankfurt-am-Main, Höchst, Germany). *Chem.-Ing.-Tech.*, 1955, **27** (10), 604-607.—A simple infra-red spectrophotometer for the determination of water is described. A disc, which is rotated by a synchro-

nous motor, and contains two interference filters transmitting light of 1.96 and 1.7 μ and whose relative transmissions are matched to the response of the lead sulphide detector, is interposed between the light source and the detector. Water absorbs more strongly at 1.96 μ , and when introduced gives rise to an off-balance a.c. current, which is amplified. The apparatus is suitable for measurement of water concn. in thin films, e.g., in plastics materials, in liquids or in gases. Water layers 1 μ thick or water vapour concn. of 1 g per cu. m can easily be measured. The circuit of the detector is given. High stability is claimed. P. S. STROSS

1248. The determination of 1:2-dichloroethane. I. F. I. Trishin, E. G. Maleeva and N. S. Skornyakova. *Trudy Odessk. Tekhnol. Inst.*, 1955, **5**, 103-111; *Ref. Zhur., Khim.*, 1956, Abstr. No. 26,017.—A study has been made of the determination of 1:2-dichloroethane (**I**) by reduction with metallic Na (**II**) in ethyl, isobutyl or isoamyl alcohol and in ethanediol. The determination was carried out in acetic acid by the action of Ca and Mg, and also by alcoholic KOH, by catalytic hydrogenation on a skeletal nickel catalyst in the presence of alcoholic KOH, and by the action of alcohols on **II**. The experiments showed that the action of alkali or an alcoholate in all alcohols on warming is to split off Cl from **I**; the higher the b.p. of the alcohol, the greater is the percentage of Cl replaced, but it is impossible to remove Cl completely, even by boiling for 10 hr. The action of **II** as an alcoholate causes removal of Cl from **I** to proceed more rapidly than the action of alkali soln. Hydrogenation of **I** in the presence of a skeletal nickel catalyst proceeds more rapidly with hydrogen obtained by the action of **II** on alcohol than with molecular hydrogen, and is the most rapid method for determining Cl in **I** (95% of Cl in 20 min.; increasing the duration of the experiment does not improve the results).

C. D. KOPKIN

1249. Modifications of the aniline acetate-furfuraldehyde method for the determination of pentose. A. Borrow and E. G. Jefferys (I.C.I. Ltd., Akers Res. Lab., The Frythe, Welwyn, England). *Analyst*, 1956, **81**, 598-601.—The method described is that of Reeves *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 551) modified to give greater sensitivity by increasing the aniline concn. and lowering the reaction temp. The pentose soln. (1 ml containing 10 to 80 μ g of pentose), in a tube calibrated at 7 ml, is heated under reflux for 2.5 hr. with 2 ml of 5.55 N HCl. The aq. layer is then removed, xylene is added to the 7-ml mark and the soln. is dried with anhydrous Na acetate. A 5-ml aliquot is cooled in an ice bath, then treated with 5 ml of cooled aniline reagent (4.5% in equal parts of ethanol and glacial acetic acid). The mixture is cooled in ice-water for 18 min. and the colour is compared spectrophotometrically at 540 m μ with that of a standard xylose soln. (50 μ g) subjected to the whole procedure. A. O. JONES

1250. Analysis for industry [colorimetric determination of aldehydes and ketones]. J. P. G. Farr *Ind. Chem. Mfr.*, 1956, **32**, 389-390.—A review of the literature is presented, including references to colorimetric determinations based on condensation of the carbonyl group with a methylene group activated by another carbonyl group, the use of dimedone, and determination of furfuraldehyde. (70 references.) S.C.I. ABSTR.

1251. Isolation and separation of mixtures of formaldehyde and acetaldehyde by means of dimedone. A. F. Lukovnikov (Inst. of Chem. Physics, Acad. Sci., U.S.S.R., Moscow). *Zhur. Anal. Khim.*, 1956, **11** (3), 299–302.—The separation of formaldehyde and acetaldehyde from each other and from mixtures with other aldehydes by the dimedone reaction is studied by the use of radioactive C. To separate the aldehydes, the mixture is treated first with aq. dimedone soln. (saturated at 20°), then, for each 50 ml, 2 g of solid dimedone and 5 ml of conc. H_2SO_4 are added, and the mixture is boiled under a reflux condenser for 3 to 4 hr. To avoid contamination with excess of reagent, the acetaldehyde derivative is filtered off from the hot solution and washed with warm NaOH soln. The formaldehyde derivative is obtained from the filtrate by addition of acid and washing the ppt. with 50% aq. ethanol.

G. S. SMITH

1252. A polarographic method for determining aldehydes in ethanol. M. S. Shul'man and O. F. Gavrikova. *Tr. Vses. Nauch. Inst. Spirit. Promyshlennosti*, 1955, (5), 176–178; *Ref. Zhur. Khim.*, 1956, Abstr. No. 43, 568.—The content of formaldehyde, acetaldehyde and furfuraldehyde in ethanol is determined polarographically in the presence of NaOH, KOH or LiOH. Ethanol is diluted to a 50 to 70% concn., to 10 ml of which 1 ml of N alkali is added; this mixture is polarographed without the removal of O. In determining acetaldehyde, LiOH is used as background; for furfuraldehyde, NH_4Cl , KOH, NaOH or LiOH; and for formaldehyde, NaOH, KOH or LiOH is used. With LiOH as background it is possible to determine acetaldehyde and furfuraldehyde together. The error is $\pm 0.0003\%$ (abs.). R. LORD

1253. Identification of ketones by catalytic Wolff-Kishner reduction of hydrazones and mass spectrometry. H. Siegel and D. O. Schissler (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1646–1648.—The carbon-chain configuration of aliphatic ketones has been determined from the fragmentation patterns in the mass spectra of the alkanes derived from them by Wolff-Kishner reduction, with the reduction apparatus illustrated.

E. G. CUMMINS

1254. Identification of silver salts of branched-chain fatty acids by X-ray diffraction powder patterns. D. L. Guertin, S. E. Wiberley, W. H. Bauer and J. Fisher (Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1645–1646.—X-ray diffraction data are tabulated for the silver salts of 13 derivatives of hexoic acid, and one derivative of heptoic acid.

E. G. CUMMINS

1255. The characterisation of fatty acids by chromatographic separation of the *p*-(4-nitrophenylazo)-phenacyl bromide. E. S. Amin and E. Hecker (Physiol.-Chem. Inst., Univ. Tübingen, Germany). *Chem. Ber.*, 1956, **89** (6), 1496–1502.—A description is given of the four-stage prep. in 81% yield of *p*-(4-nitrophenylazo)phenacyl bromide (**I**) starting from *p*-(4-nitrophenylazo)acetophenone. When crystallised from acetone, benzene or ethanol, **I** has a m.p. of 182°; it reacts with the sodium salts of fatty acids in a mixture of dioxan with tetrahydrofuran or in ethanol to form deep-red esters, which crystallise from benzene, ethanol or acetone and have

characteristic m.p. and extinctions. These esters can be separated on a kieselguhr column (Amin and Hecker, *Ibid.*, 1956, **89**, 695) with a variety of solvents, of which six examples are given; four of them are based on cyclohexane with one or two other solvents and the other two are based on octane and decane, respectively. Curves are given to show the clear separation of *n*-octoic, *n*-hexoic and lauric acids from a mixture of all three.

P. HAAS

1256. Identification of amines as tetraphenylborates. F. E. Crane, jun. (Douglass Coll. Chem. Lab., Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1794–1797.—A 0.6% aq. soln. of Na tetraphenylboron causes an immediate pptn. of the corresponding salt of any basic amine. Two quaternary -onium salts (diethylmethylsulphonium iodide and S-benzylthiuronium chloride) also give ppt. Non-basic amines such as nitro-anilines are ptdt. slowly or not at all; ethanamine with a solubilising group is not ptdt. Melting-points of the ppt. are recorded. To determine the tetraphenylboron in the ppt., 0.2 to 0.4 mill-equiv. is dissolved in aq. acetone (1:1) and a mixture of 3 ml of 3 M acetic acid and 3 ml of 3 M Na acetate is added. The soln. is then titrated with 0.06 N aq. $AgNO_3$, with a silver indicator and glass reference electrodes.

E. J. H. BIRCH

1257. Identification of aliphatic and aromatic primary amines by means of *o*-diacetylbenzene. F. Weygand, H. Weber, E. Maekawa and G. Eberhardt (Org.-Chem. Inst. Tech. Univ., Berlin-Charlottenburg). *Chem. Ber.*, 1956, **89** (8), 1994–1999.—To prepare the reagent, ethylbenzene is nitrated to the *o*- and *p*-derivatives, the former of which is reduced by Raney nickel and H; the resulting amine is diazotised in the presence of KI to form *o*-ethyliodobenzene. This is submitted to a Grignard reaction with acetaldehyde to form a carbinol which, without isolation, is directly oxidised by CrO_3 to *o*-ethylacetophenone, which is further oxidised by 75% $KMnO_4$ (Riemschneider and Weygand, *Monatsh.*, 1955, **86**, 201) to *o*-diacetylbenzene (m.p. 38°). *o*-Diacetylbenzene gives a colour reaction with primary amines. An aq. soln. of the reagent added to an aq. soln. of the amine in the presence of 5% $NaHCO_3$ produces, during 5 to 15 min., a pink or violet colour, or, after acidification with acetic acid and warming, a definite violet colour. The range of concn. detectable by paper chromatography is given as 1 to 10 μ g for some aromatic primary amines.

P. HAAS

1258. Titration of hydrazine and its derivatives with sodium nitrite. J. Vulterin and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (3), 364–369.—In acid solution, hydrazine reacts quantitatively with $NaNO_2$. This reaction was used for the volumetric potentiometric determination of hydrazine in 7 to 10% HCl, 15 to 30% $HClO_4$, 50% H_3PO_4 or 10 to 12% H_2SO_4 . Phenylhydrazine in 10% HCl, semicarbazide in 10 to 15% HCl, 18% H_2SO_4 or 53% H_3PO_4 , and thiosemicarbazide in 1 to 5% HCl, 1 to 5% H_2SO_4 , 20 to 30% H_3PO_4 or 1 to 15% $HClO_4$ can be titrated in a similar manner. The stoichiometric relations are discussed and equations formulated. In investigating the stability of $NaNO_2$ as a volumetric reagent, it was found that 0.1 M as well as 0.01 M solutions are stable for several weeks.

J. ZÝKA

3.—ORGANIC ANALYSIS

1259. The analysis of mixtures of the hydrochlorides of hexamethylenediamine, *p,p'*-diaminodicyclohexylmethane and ϵ -aminocaproic acid. M. Clasper, J. Haslam and E. F. Mooney (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *Analyst*, 1956, **81**, 587-594.—In the method described, the soln. of the mixed hydrochlorides is applied to a cellulose column, with *sec*-butyl alcohol-formic acid-water as eluting solvent. The eluate contains ϵ -aminocaproic acid hydrochloride and *p,p'*-diaminodicyclohexylmethane dihydrochloride. The column is then eluted with ethanol-water (75 + 25) and the eluate contains the hexamethylenediamine dihydrochloride. The procedures for determining the hydrochlorides in the two fractions are described.

A. O. JONES

1260. Polarographic determination of vinyl cyanide in aqueous alcoholic solutions. M. N. Platanova (S. M. Budennii Engng Acad.). *Zhur. Anal. Khim.*, 1956, **11** (3), 310-312.—In 0.01 M tetraethylammonium chloride (50% aq. ethanol soln.), vinyl cyanide (0.3 to 12.04 millimoles) gives a polarographic wave with $E_{\frac{1}{2}} = 2.05$ V *vs.* the S.C.E. The height is proportional to the concn. Reduction at the dropping-mercury electrode is irreversible and occurs at the double bond, giving the nitrile of acetic acid.

G. S. SMITH

1261. Identification of organic compounds. XI. The addition compounds of aliphatic sulphides with mercuric halides. M. Večerá, J. Gasparič, D. Snobl and M. Jureček (Res. Inst. Org. Synth., Pardubice-Rybítví, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 770-778.—The preparation and properties of addition compounds of organic sulphides with mercuric halides were studied, but only the addition compounds with mercuric chloride were found to be suitable for identifying purposes. The corresponding deriv. of 28 aliphatic sulphides having C_1 to C_4 alkyl groups, with the exception of *tert*-butyl deriv., were prepared, and the possibility of their being identified by means of X-ray methods was investigated; their m.p. and physical properties are given.

J. ZÝKA

1262. Selenosemicarbazide and its derivatives. III. Rapid method of determining selenium in selenosemicarbazones. R. Huls and M. Renson (Lab. de Chim. Organ., Univ. de Liège, Belgium). *Bull. Soc. Chim. Belg.*, 1956, **65** (7-8), 696-699.—Selenosemicarbazone (0.01 g) is dissolved in 5 ml of ethanol and acidified with 2.5 ml of *N* HNO_3 ; 0.01 *N* aq. $AgNO_3$ (10 ml) is added and the white flocculent ppt. formed is converted into the black Ag_2Se by being heated on a water bath for 10 to 15 min. When the suspension is cool, nitrobenzene (2 to 3 ml) is added to cover the ppt. and the excess of $AgNO_3$ is titrated with 0.01 *N* aq. $KSCN$ (about 5 ml) by the Volhard method. The average error in determinations on 30 different substances is $\pm 1\%$.

A. JOBLING

1263. Determination of di- and tri-alkyl phosphites in the presence of each other. D. N. Bernhart and K. H. Rattenbury (Res. Lab., Victor Chem. Works, Chicago Heights, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1765-1766.—Dialkyl phosphites are hydrolysed to sodium monoalkyl phosphites in alcoholic $NaOH$, 1 mol per mol. being consumed within 1 min., whereas trialkyl phosphites are not hydrolysed under these conditions within 10 min. In an acid medium, trialkyl phosphites are hydrolysed to dialkyl phosphites. Methods of

determination based on these reactions are described. Alcohols, amine hydrochlorides and dialkyl alkanephosphonates do not interfere. The method has been tested with esters ranging from butyl to octyl phosphites.

E. J. H. BIRCH

1264. Determination of the dichlorobenzene isomers. A. A. Sprýškov and Yu. G. Erýkalov (Ivanovo Chem.-technol. Inst.). *Zhur. Anal. Khim.*, 1956, **11** (4), 492-494.—The para isomer in a mixture of the three isomers of dichlorobenzene can be determined by the solidifying-point method of van der Linden (*Rec. Trav. Chim. Pays-Bas*, 1911, **30**, 305). The meta isomer can be determined by nitration, reduction and bromination of the mixture. Nitration and reduction give five isomeric dichloroanilines. The amines from *m*-dichlorobenzene give monobromo derivatives and those from *o*- and *p*-dichlorobenzene give dibromo derivatives. From titrations with bromide-bromate the amount of *m*-dichlorobenzene can therefore be calculated. The amount of *o*-dichlorobenzene is calculated by difference.

G. S. SMITH

1265. Vapour-phase chromatographic determination of benzene, naphthalene and other hydrocarbons in wash-oil. Application of a simple and accurate detection method for vapour-phase chromatography. L. Blom and L. Edelhausen (Staatsmijnen in Limburg, Central Lab., Geleen, The Netherlands). *Anal. Chim. Acta*, 1956, **15** (6), 559-566.—Procedures and apparatus for the rapid determination of from 0.1 to 0.6 g of benzene and from 0.5 to 30% of naphthalene per litre of wash-oil are described. Toluene, xylene and the methylnaphthalenes can be determined simultaneously. Part of the benzene is removed from the dry oil in a stream of *N* (0.6 litre per hr. for 15 min.) at 100°, and is collected in a receiver at -40° connected to a spiral chromatographic column (3 m) filled with sterchamol impregnated with dinonyl phthalate and heated to $\approx 80^\circ$. The separated benzene (containing $\approx 2\%$ of thiophen) is then burnt at 700° in a silica tube packed with CuO , and the CO_2 is titrated immediately in pyridine soln. with 0.1 *N* Na methoxide. To obtain the benzene content of the sample, the amount of benzene removed is multiplied by a factor (between 400 and 460) determined for wash-oils of different known benzene concn. In the determination of toluene and xylene, the column is kept at 100°. The naphthalene content is determined directly by passing the sample through a spiral column (6 m long) filled with sterchamol impregnated with silicone grease and heated electrically at 200°. A stream of O-free *N* is passed through the column at a rate of 2 litres per hr. and the O for combustion of the hydrocarbons is injected (1.5 litres per hr.) at the front of the silica tube, which is heated to 800°. The initial fraction is almost pure naphthalene and the following fraction contains the methylnaphthalenes. The accuracy and reproducibility are satisfactory for routine analyses.

W. J. BAKER

1266. Precision and accuracy of spectrophotometric analysis of binary systems. I. General formulae for precision of determinations. J. Świętosławska (Inst. of Gen. Chem., Warsaw). *Roczn. Chem.*, 1956, **30** (2), 570-585.—The relative errors incurred in spectrophotometric analysis of binary mixtures in non-absorbing solvents become large when $mn \approx 1$, and are small when $mn \rightarrow 0$, where $m = k_{11}/k_{21}$ and $n = k_{21}/k_{22}$, and k_{11} and k_{22} are the absorption coefficients of the first, and k_{21}

and k_{22} of the second, component, at two given wavelengths. The accuracy of determination of a component falls with rise in relative concn. of the other component. Expressions for calculating the analytical error are derived, for variable m and n and concn. of the components.

II. Determination of carbazole and anthracene in their equimolecular mixtures. J. Świetłowska. *Ibid.*, 1956, **30** (2), 587-605.—Satisfactory agreement is obtained between experimental and calculated values for the analytical error of spectrophotometric determination of carbazole and anthracene in ethanol. The accuracy of the analysis does not depend solely on the precision of the measurements.

R. TRUSCOE

1267. The determination of phenols by chromatography and spectrophotometry of their methyl ethers. I. Ultra-violet absorption spectra of methyl aryl ethers in cyclohexane. B. T. Commins and A. J. Lindsey (Sir John Cass Coll., London). *Anal. Chim. Acta*, 1956, **15** (5), 446-450.—The u.v. absorption spectra of 16 methyl aryl ethers have been determined with a view to their use in the determination of the corresponding phenols.

II. Separation and quantitative determination of methyl aryl ethers. B. T. Commins and A. J. Lindsey. *Ibid.*, 1956, **15** (6), 551-554.—The quant. methylation of phenols in microgram amounts and the chromatographic separation of the methyl aryl ethers by elution with cyclohexane on alumina columns (2.5 to 30 cm \times 1 cm) are described. The amounts of the separated ethers can be determined by u.v. spectrophotometry of each eluate in a 1-cm quartz cell (slit width 0.3 mm), a "standard optical height" (given) being used for each compound. The accuracy is usually within 5%; data for guaiacol, anisole, methyl tolyl ethers, methyl xylyl ethers, dimethoxybenzenes and methyl naphthyl ethers are given.

III. Determination of phenols in wood smoke. B. T. Commins and A. J. Lindsey. *Ibid.*, 1956, **15** (6), 554-556.—The procedures described in Part II can be applied to the determination of phenol, *o*-, *m*- and *p*-cresol, 1- and 2-naphthol, catechol, resorcinol and quinol in wood smoke, e.g., for curing fish. The smoke is trapped at -80° and dissolved in ethanol; the phenols are removed by successive extractions with CHCl_3 containing 5% of ethanol, and are then re-extracted into 2 N NaOH for methylation. An aliquot of the cyclohexane soln. of the methyl aryl ethers is passed through a 11-cm column of Al_2O_3 containing 1% of added H_2O to separate the deriv. of phenol and cresols; another aliquot is eluted through a 2.5-cm column of Al_2O_3 containing 5% of added H_2O to separate the dimethoxybenzenes. The naphthyl ethers are obtained by a second separation of the dimethoxybenzenes on a similar column. The spectrophotometric determinations on the successive eluates are made as described in Part II. Guaiacol is also present.

IV. The determination of phenols in cigarette smoke. B. T. Commins and A. J. Lindsey. *Ibid.*, 1956, **15** (6), 557-558.—The various phenols in cigarette smoke can be separated and determined by the extraction, methylation, elution and spectrophotometric procedures described previously (cf. Parts II and III, above). The three isomeric dihydroxybenzenes are probably present partly as their monomethyl ethers; a method of determining these is being developed. Guaiacol ($\approx 6\%$ of total phenols) is reported as catechol.

W. C. JOHNSON
W. J. BAKER

1268. Chromatography of aromatic isomers. V. Quantitative determination of the xylenols and ethylphenols by partition chromatography on silica gel. J. Franc (Res. Inst. Org. Synth., Pardubice-Kybítiv, Czechoslovakia). *Chem. Listy*, 1956, **50** (4), 547-552.—A quant. method for the determination of xylenols, ethylphenols and cresols in the technical xylene fraction is described. After separation by partition chromatography on silica gel with cyclohexane - H_2O , 2:6-xylene, the mixture of 2:5- and 2:3-xylene, 3:5-xylene, *m*-ethylphenol, *o*- and *m*-cresols and phenol can be determined photometrically in the eluate. A soln. of 2:6-dichloro-*p*-benzoquinonechlorimine was used as reagent. Phenols substituted in the *para*-position do not react. The validity of the relationship between R_F value and dipole moment of the separated isomers, stated in previous papers, has also been proved for partition chromatography on silica gel. J. ZÝKA

1269. Bromimetric determination of 2:2-di-(*p*-hydroxyphenyl)propane with amperometric end-point indication. V. Ulbrich (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 743-747.—With 0.1 M KBrO_3 as volumetric soln. and a rotating platinum electrode as indicator electrode, an amperometric determination of 2:2-di-(*p*-hydroxyphenyl)propane (**I**), alone or in admixture with 1-chloro-2:3-epoxypropane in the presence of condensation products, has been developed. The method was also used for studying the velocity of condensation of **I** with 1-chloro-2:3-epoxypropane. A mixture of dimethylformamide (25 ml), methanol (15 ml), H_2O (10 ml) and HCl (1:1) (5 ml) was used as solvent and titrating medium. When titrating 2.2×10^{-5} M and 1.7×10^{-4} M soln. of **I** the errors did not exceed 5% and $\pm 0.6\%$, respectively. J. ZÝKA

1270. High-frequency titrations of some substituted anilines in glacial acetic acid. W. T. Lippincott and A. Timnick (Kedzie Chem. Lab., Michigan State Univ., East Lansing, U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1690-1692.—High-frequency (130 Mc) titration of 11 substituted anilines in glacial acetic acid with HClO_4 in glacial acetic acid are compared with potentiometric and conductimetric titrations, and fair agreement is obtained. For *p*-aminoacetophenone the high-frequency titration is superior. None of the methods gives a satisfactory result with 2:4-dinitroaniline. Mixtures of two amines were also titrated, but results were unsatisfactory for *o*- and *p*-nitroaniline, *m*- and *p*-nitroaniline, and *m*- and *p*-toluidine. It appears that bases of the same basic strength but differing in mol. wt. by > 15 units are resolvable.

E. J. H. BIRCH

1271. Determination of tertiary amines in xylidine fractions by use of infra-red spectra. I. Detection and determination of 2:3:4:6-tetramethylpyridine. Shigeyuki Tanaka and Hisakazu Arakawa (Inst. Techno-anal. Chem., Faculty of Eng., Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1956, **5** (8), 455-458.—The xylidine fraction of coal tar is fractionated by vacuum distillation and liquid-liquid extraction with benzene and $N\text{HCl}$. 2:3:4:6-Tetramethylpyridine was identified in the most basic fraction through its i.r. absorption bands at 7.2, 8.2, 9.9, 10.5 and 11.7 μ . The extinction of its CS_2 soln. at 11.68 μ is proportional to concn. of $< 8\%$, the standard deviation being $\approx 1\%$. Its content in crude xylidine was $\approx 7\%$. K. SAITO

3.—ORGANIC ANALYSIS

1272. Determination of esters of isonicotinic and nicotinic acids by ultra-violet absorption spectroscopy. Nobuo Soma (Takamine Lab., Sankyo Co. Ltd., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1955, **7**, 97-102.—The absorption spectra of methyl, ethyl and butyl esters of picolinic (**I**), nicotinic (**II**) and isonicotinic (**III**) acids were measured in ethanolic soln. No significant difference was found between the methyl and ethyl esters. **I** and **II** give similar absorption, which is different from that of **III**. Ethyl esters of **II** and **III** are determined in their mixture by the use of two key bands at 229 and 285 m μ . Their butyl esters are also determined with the aid of two key bands at 230 and 285 m μ . The error is <0.5%. K. SAITO

1273. Application of nitrometry. XI. Determination of 8-oxocamphor [1:7-dimethyl-2-oxonorcamphane-7-aldehyde]. Masaharu Yamagishi, Makoto Yokoo and Saburō Inoue (Res. Lab., Takeda Pharm. Ind. Ltd., Juso-nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (11), 1383-1384.—8-Oxocamphor (**I**) (1 to 6 mg per ml) (1 ml) reacts with 2:4-dinitrophenylhydrazine (**II**) (7 to 10 mg per ml) (20 ml) in *N* HCl in a 1 to 1 ratio; the excess of **II** is determined by nitrometry with iodine soln. (5 g per 20 ml of water containing 20 g of KI) (*Anal. Abstr.*, 1956, **3**, 2144). *iso*-Ketopinic acid [1:7-dimethyl-2-oxonorcamphane-7-carboxylic acid] and 8-hydroxycamphor fail to react with **II**; 3- and 5-oxocamphor react only very slowly, not interfering with the determination of **I**.

XII. Utilisation of Nessler reagent in nitrometry. Masaharu Yamagishi, Makoto Yokoo and Saburō Inoue. *Ibid.*, 1956, **75** (11), 1384-1386.—Since Hg²⁺ react with hydrazine in a basic soln. to give N equiv. in amount to the Hg, nitrometry is applied to the analysis of aldehydes by the Gowani method (*J. Ind. Chem. Soc.*, 1935, **12**, 714; 1936, **13**, 315). The sample (0.1 to 0.7 mg in 1 ml) is treated with Nessler reagent (**III**) (200 mg of HgCl₂ and 650 mg of KI per 100 ml) and introduced into a nitrometer with saturated NaCl soln. Ketones and aromatic hydroxyaldehydes such as vanillin and salicylaldehyde fail to react with **III**, whilst their alkyl ethers such as anisaldehyde as well as hydroxyketones (such as ketoses or benzoin) react with **III** on heating. K. SAITO

1274. 4-Phenyl-2:6-di-(4-phenyl-2-pyridyl)- and 4-phenyl-2:6-di-(6-phenyl-2-pyridyl)-pyridine. Their spectrophotometric constants in reactions of chelation with Fe(II), Cu(I) and Co(II). A. A. Schilt and G. F. Smith (Univ. of Illinois, Urbana, Ill., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (6), 567-572.—Values of the max. extinction (λ_{max}) and mol. extinction coeff. (ϵ) are reported and discussed for some metal chelates of two triphenyl deriv. of 2:6-di-(2-pyridyl)-pyridine (terpyridine) (*cf.* *Anal. Abstr.*, 1954, **1**, 320). The Fe^{II} complex of 4-phenyl-2:6-di-(4-phenyl-2-pyridyl)pyridine (terosite) has λ_{max} at 383 m μ (ϵ , 21,000) and 583 m μ (ϵ , 30,000); the Co^{II} complex has λ_{max} at 466 m μ (ϵ , 3000) and 528 m μ (ϵ , 3100). Both coloured complexes are very stable (between pH 2 or 4 to 8) and are sol. in CHCl₃ or in CHCl₃ and ethanol (1:1); because of this and the high specificity and sensitivity of the reactions, terosite can be used as chelation agent for the simultaneous determination of Fe²⁺ and Co²⁺ by measuring the extinctions at 583 and 450 m μ . The highly coloured Cu^I complex of 4-phenyl-2:6-di-(6-phenyl-2-pyridyl)pyridine has λ_{max} at 423 m μ (ϵ , 4500) and 567 m μ (ϵ , 3200); these low values

of ϵ and the absence of any complex with Fe^{II} or Co^{II} differentiate the above-mentioned triphenyl deriv. of terpyridine. The Cu^I complex is stable between pH 2 and 8.2 and is also sol. in a mixture of CHCl₃ and ethanol (1:1). W. J. BAKER

1275. Dichromate method of determining piperazine. A. A. Chemerisskaya (S. Ordzhonikidze All-Union Sci. Res. Chem.-Pharm. Inst.). *Zhur. Anal. Khim.*, 1956, **11** (3), 356.—Improvements in the method of Castiglioni *et al.* (*Brit. Abstr. C*, 1953, 352) are described. The complex formed is almost certainly C₄H₁₀N₂Cr₂O₇ and not C₄H₈N₂Cr₂O₇. The time of standing after addition of CrO₃ can be shortened from several hours to 15 min. by cooling the reaction mixture with ice after the addition of 2 ml of 40% CrO₃ soln. G. S. SMITH

1276. The determination of hydrogen [in natural gas] by ignition over copper oxide. V. P. Rozhestvenskii. *Uch. Zap. Saratov. Univ.*, 1955, **42**, 109-112; *Ref. Zhur. Khim.*, 1956, Abstr. No. 36,178.—The conditions are studied for the determination of H in natural gas and its mixtures by ignition over CuO in the modified apparatus of the Vsesoyusnyi Teplotekhnicheskii Institut. Instead of a U-tube with CuO for the oxidation of CO and H and an explosion pipette for the oxidation of C_nH_{2n+2}, a porcelain tube filled with CuO is used. The ignition temp. is lowered to 265°, for at the earlier recommended temp. of 280° to 300° part of the higher hydrocarbons burns to CO₂ and the results in the determination of H are erroneous. Electrolytic H burns completely at 260° to 265°, and C_nH_{2n+2} in samples of natural gas is not oxidised. Reproducibility of results and the agreement between calculated and experimental figures are good. Complete burning of methane takes place only above 850°. C. D. KOPKIN

1277. The structural analysis of petroleum products by infra-red absorption spectra. K. I. Zimina, A. V. Iogansen and A. G. Siryuk. Report of Symposium: "Metody Issledov. Neft. Nefteprodukt., M., Gostoptekhizdat," 1955, 223-235; *Ref. Zhur. Khim.*, 1956, Abstr. No. 36,217.—Several uses of infra-red spectroscopy are discussed. In particular it is shown that, of the samples of resinous substances from petroleum that were studied, a characteristic is the presence of >C=O groups; in the deparaffinisation of kerosene by direct distillation of eastern petroleum with urea, both *n*- and isoparaffin hydrocarbons are obtained; in the deparaffinisation of kerosene from thermal cracking with urea, no removal of α -olefins takes place; unsaturated hydrocarbons of various types are obtained in the same proportions as in the original product; in petrol from catalytic cracking the following types of unsaturated hydrocarbons have been established—RR'C:CHR'', trans-RHC:CHR' and RR'C:CH₂. C. D. KOPKIN

1278. Rapid method for simultaneous determination of sulphur and phosphorus in petroleum products. P. B. Gerhardt and G. V. Dyroff (Esso Res. and Engng Co., Products Res. Div., Linden, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1725-1728.—The sample, mixed with a large excess of ZnO, is heated under O and the resulting SO₂ is absorbed in acid I⁻ soln. containing starch, the colour of which is maintained by addition of standard IO₃⁻. The P in the combustion residue is extracted in H₂SO₄ and to the soln. is added dil. ammonium vanadate

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[Abstr. 1279-1285]

and molybdate soln. The intensity of the colour is measured in a spectrophotometer and compared with standards. Typical analytical, including precision, data are presented. D. A. PANTONY

1279. Separation of porphyrins [from petroleum sediments] by paper chromatography. M. Blumer (Exploration and Prod. Res. Div., Shell Development Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1640-1644.—The conditions under which the porphyrins and metal porphyrin complexes found in petroleum and ancient sediments can best be separated by paper chromatography are investigated. The chromatograms are run horizontally in a solvent-saturated enclosure and the best conditions are found to be—a solvent comprising 50 to 70% of CCl_4 in isoctane (2:2:4-trimethylpentane) if only aetioporphyrins have to be resolved, or 70 to 85% of CCl_4 in isoctane if esters have to be resolved, and Whatman No. 3 paper. For separation of acid porphyrins, a two-dimensional chromatogram is run, first in one direction, leaving the acid porphyrins at the origin and separating, in the order of increasing R_F , dimethylproporphyrin, dimethylmesoporphyrin, methyl deoxophylloerythrin, deoxophylloerythro-aetioporphyrin - vanadium complex, deoxophylloerythro-aetioporphyrin and its nickel complex and mesoaeioporphyrin. The acid spot at the start is then esterified with diazomethane in cyclohexane soln. and the chromatogram is run again with the same solvent at right angles, separating the acids as their methyl esters. The free porphyrins are detected by their fluorescence in u.v. light and the metal complexes by impregnating with fluoranthene and exposing to u.v. light; the metal-complex spots inhibit fluorescence. The useful limits of concn. are 0.5 to 0.005 μg for the free and 0.5 to 0.04 μg for the metal-complexed porphyrins. The method can be used semi-quantitatively and the relationship between structure and R_F is discussed. E. J. H. BIRCH

1280. Determination of carbon-type composition and molecular weight of mineral-oil fractions from viscosity, refractive index and density by means of nomograms. J. Cornelissen and H. I. Waterman (Technol. Univ., Delft, Netherlands). *Anal. Chim. Acta*, 1956, **15** (5), 401-409.—Six nomograms are reproduced to enable the percentage of carbon in aromatic rings, the percentage of carbon in naphthenic rings and the average mol. wt. to be determined from the viscosity, refractive index and density of mineral-oil fractions. Each nomogram relates to one viscosity value, and intermediate viscosities are dealt with by linear interpolation of the readings. W. C. JOHNSON

1281. Simple method for the detection of paraffin wax in wax mixtures. II. W. Hessler (Werner u. Mertz, A.-G., Mainz). *Fette, Seif., Anstrichmitt.*, 1956, **58** (8), 602.—The detection of paraffin wax in wax mixtures by treating a sample with saturated urea soln. and observing whether chalky outgrowths are formed (*Anal. Abstr.*, 1956, **3**, 3112) gives negative results with some samples of montan wax containing paraffin wax. If the test is carried out at a temp. 15° to 20° below the m.p. of the wax, and the surface of the sample is roughened before the reagent is applied, all waxes containing paraffin wax give positive results. E. HAYES

1282. The determination of traces of manganese in textiles by means of formaldoxime. A. G. Hamlin (British Cotton Industry Res. Ass., Shirley Inst., Didsbury, Manchester). *J. Text. Inst. Trans.*

1956, **47** (8), 1445-1452.—The investigation described shows that the formaldoxime method can be used for the colorimetric determination of Mn in textiles if Fe, Ti, Zr, MoO_4^{2-} and VO_3^- are removed by extraction of the cupferron complex with dichloromethane and if Co, Cu and Ni are masked by cyanide. Interference by borate ions is overcome by adding a large excess of formaldoxime reagent (20 ml in the presence of 100 mg of boric acid); Cr^{3+} (1 to 2 mg) by previous pptn. of the Mn as dioxide, with Fe(OH)_3 as collector; Co by leaving the alkaline soln. to stand for 30 min.; and Cu^{2+} (> 5 mg) by extracting the Fe, adding Na diethylthiocarbamate to the soln., and extracting the brown copper complex with dichloromethane. If phosphate is present with Ca or Mg or both, the soln. must contain 20 to 25% (w/v) of ammonium salts after dilution, and 2 g of $\text{Na}_4\text{P}_2\text{O}_7$ must be added before making the soln. alkaline. If phosphate is present with Pb, the Pb is separated before the Mn is determined. The method is not as simple as those based on oxidation of the Mn to HMnO_4 , but it is equally widely applicable and about five times more sensitive. O. M. WHITTON

1283. Determination of micro quantities of sulphate ion derived from small samples of textile material. J. M. Bather (British Cotton Industry Res. Ass., Shirley Inst., Didsbury, Manchester). *Shirley Inst. Mem.*, 1956, **29** (12), 115-117.—The method of Belcher *et al.* (*Anal. Abstr.*, 1954, **1**, 448) has been modified to permit the rapid determination of SO_4^{2-} in the range 0.1 mg to 2 mg. The chief improvement is in the filtration procedure, a filter-paper pad deposited on the disc of a porous porcelain filter-stick being used. The SO_4^{2-} are ptd. as BaSO_4 , which is then dissolved in EDTA, the excess of solvent being titrated with standard MgCl_2 soln. As many as 12 determinations per day can be made. A. M. SPRATT

1284. Determination of the hydrophile - lipophile character of surface-active agents and oils by a water titration. H. L. Greenwald, G. L. Brown and M. N. Fineman (Rohm & Haas Co., 5000 Richmond St., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1693-1697.—The hydrophile - lipophile balance of an emulsifying agent is gauged as a water no. by weighing a 1-g sample of the substance into a flask, adding 30 ml of a selected solvent and titrating with water to a persistent turbidity (not a mere cloud). The most suitable solvent for the octyl phenyl polyoxyethylene series was found to be dioxan containing 4% of benzene. Commercial dioxan is somewhat variable in composition so that, in practice, benzene is added until the solvent gives the standard water no. (21.6 to 21.8 ml) when titrated alone. The water no. so obtained correlates, though not perfectly, with the hydrophile - lipophile balance determined in other ways and would act as a guide for emulsifier selection. E. J. H. BIRCH

1285. Applications of spectrophotometry in the analysis of citrus essential oils. F. La Face and M. D. Riganesi (Centro Studio Essenze, Reggio, Calabria, Italy). *Ric. Sci.*, 1956, **26** (3), 819-824.—Two procedures for the analysis of lemon oils have been compared, the Palermo procedure (ratio of transmissions at 290, 310 and 340 μm) and the American procedure (comparison of absorption at the max. at 315 μm with that at two inflection points at ≈ 285 and $\approx 365 \mu\text{m}$). Two commercial synthetic lemon oils were found to behave spectrophotometrically like natural oils according to the

American procedure, but abnormally according to the Palermo procedure. The evaporation residue of natural oils (max. at 314 and 249 m μ) was found to have a significantly different spectrum from that of the synthetic oils (single max. at 319 m μ). The spectra of some sweet-orange oils (max. at 329 m μ) have also been studied, and the contribution of the residue to the spectrum was found to be of importance.

L. A. O'NEILL

1286. Spectroscopic investigation of essential oils. I. Quantitative evaluation of sandalwood oil by infra-red spectroscopy. V. K. Balakrishnan, S. Dasgupta and S. C. Bhattacharyya (Nat. Chem. Lab. of India, Poona). *Perfum. Essent. Oil Rec.*, 1956, **47** (11), 383-390.—The principal constituents of Indian sandalwood oil are α - and β -santalol. α -Santalol contains a fused cyclopropane ring, and this structure in sandalwood oil shows a characteristic max. absorption at 3-27 μ and 9-98 μ , which can be used for the direct assessment of the quality of sandalwood oil. In order to eliminate the interference of -OH groups, determinations are made on the original oil and after acetylation. On the original oil at 3-27 μ the mean specific extinction coefficient is 0-1020, and at 9-98 μ is 0-7153. The acetylated oil shows corresponding maxima at 3-25 μ and 9-88 μ , the specific extinction coefficients being 0-08095 and 0-55005, respectively. Data were obtained on oil smears and on soln. in CS₂.

H. B. HEATH

1287. The estimation of dithiodiglycolic acid in [cosmetic] preparations based on thioglycolic acid. M. Pesez (Dept. Anal. Roussel-Uclaf, Romainville, France). *Ann. Falsif.*, 1956, **49**, 403-407.—Methods described for the estimation of dithiodiglycolic acid (**I**) in the presence of thioglycolic acid (**II**) are applied to cosmetic preparations and are used to show that existing official limits for **I** are not attainable in commercial products. *Procedure*—(a) Weigh > 2 g of sample containing 50% of the ammonium salt of **II** into a 100-ml flask and dilute to 100 ml with cooled boiled water. Mix 25 ml of this soln. with water (50 ml) and conc. HCl (2.5 ml) and titrate with 0.1 N *I* soln. To a second portion of the sample soln. (50 ml) add mercuric chloride soln. (0.5%) (10 ml), conc. HCl (5 ml) and zinc dust (0.5 g). Mix for a few min., warm at 30° for 30 min., cool to 15° and dilute to 100 ml with cooled boiled water. Filter the mixture and titrate 50 ml of the filtrate as before. The difference in the titrations is equivalent to the amount of **I** present. (b) *Preparation of reduction column*—To 200 ml of a soln. of mercuric nitrate (2%) add HNO₃ (sp.gr. 1.39) (2 ml) and zinc dust (retained between Afnor sieves No. 27 and 28) (200 g). Gently agitate the mixture for 5 min., then decant the liquid and wash the amalgam with water (\times 3). Prepare a column of amalgam (15 cm \times 2.2 cm), wash with water (500 ml) and activate with 3 N acetic acid (10 ml), retaining 2.5 cm of the acid above the column. Weigh 0.5 g of the sample into a conical flask, add boiled water (20 ml), cool and titrate with 0.1 N *I* soln. Add water (30 ml) and conc. acetic acid (25 ml), pour the whole of the mixture through the reaction column and regulate the flow to complete the experiment in 2 hr. Wash the flask, first with 3 N acetic acid (15 ml), passing the washings through the column (15 min.), then with water (2 \times 50 ml). Pour the water quickly through the column. Mix the soln. and washings and titrate with 0.1 N *I* soln. as before. The difference in the titrations is equivalent to the amount of **I** present.

D. G. FORBES

1288. Detection of phenolic resins in paintings. M. Verzele (Ghent Univ., Belgium). *Chem. Weekbl.*, 1956, **52**, 335-339.—A technique for the examination of fragments of paintings is described. An initial treatment with solvent is carried out to remove the upper varnish layer. The paint coats are then treated with aq. KOH. Drying oil rapidly dissolves and white lead pigment is characterised by an initial yellow colour due to the formation of PbO, which eventually goes into solution as K₂PbO₂. By ultra-violet spectroscopic examination, an estimate of the drying-oil content may be obtained from the absorption at 275 m μ , and any low-mol.-wt. phenolic compounds detected. In the residue from the alkali treatment, phenolic resins may be detected by the vanillin test and by infra-red spectroscopic examination in a potassium bromide pellet (particularly from the doublet at \approx 1600 cm⁻¹).

L. A. O'NEILL

1289. Colorimetric agglutination method for estimation of tannin. F. Gistrner, A. Bopp and H. Hopmann (Pharm. Inst., Univ. of Bonn, Germany). *Arch. Pharm., Berlin*, 1956, **289** (4), 188-196.—A colorimetric method is described for the estimation of tannin and non-tannin material, in which the latter can be separately determined after the agglutination of the tannin. The combined tannin and non-tannins are estimated by refluxing 20 to 100-mg portions of the drug with 100 ml of 15% ethanol for 15 min., then the solvent is removed by distillation and the aq. residue is treated with NaCl (0.9 g) to produce a physiological saline soln., which is set aside overnight. The soln. is filtered and made up to 100 ml. A 1-ml aliquot is diluted to 10 ml with physiological saline soln. and a 1-ml aliquot is treated with 0.5 ml of a tungstophosphoric acid reagent (100 g of sodium tungstate in 80 ml of H₃PO₄ and 1 litre of water) and made up to 10 ml with 15% Na₂CO₃ soln. The resulting blue coloration is measured photometrically. Tannin may be pptd. by treating 1 ml of the isotonic soln. with 5 ml of a blood-corpuscle suspension, mixing and allowing to stand for 12 hr. at 15° to 20°, when agglutination occurs and the tannin separates. The non-tannin material may then be determined on the supernatant liquid.

G. R. WHALLEY

1290. Proposed official method for the assessment of fastness-to-washing of leather. Fastness Tests Committee of the Society of Leather Trades' Chemists. *J. Soc. Leath. Tr. Chem.*, 1956, **40** (6), 183-184.—Dyed leather with or without a pigment finish is washed five times in soap solution of specified strength, being rinsed after each wash. After drying at 60°, the change in the specimen is assessed by means of the standard grey scale.

B. R. HAZEL

1291. Proposed official method for the determination of fastness-to-daylight of coloured leather. Fastness Tests Committee of the Society of Leather Trades' Chemists. *J. Soc. Leath. Tr. Chem.*, 1956, **40** (6), 184-190.—The proposed method is based on B.S. 1006: 1955, "Fastness-to-daylight of coloured textiles." The test specimen and a standard pattern are partially covered by an opaque card and exposed to daylight, until fading is noted. Fading is assessed according to the standard grey scale.

B. R. HAZEL

1292. Proposed official method for the determination of colour tolerance. Colour Measurement Committee of the Society of Leather Trades' Chemists. *J. Soc. Leath. Tr. Chem.*, 1956, **40** (6), 191-194.—The proposed method is described for calculating

4.—BIOCHEMISTRY

[Abstr. 1293-1298]

colour tolerance representing a just noticeable difference under normal viewing conditions, from a determination of the colour of the sample on a photo-electric surface colorimeter. Tolerance is calculated in terms of chromaticity and luminance
B. R. HAZEL

1293. Detection and estimation of lignosulphonates in vegetable tannin blends. Sub-Committee of the American Leather Chemists Association (A.L.C.A., Tanners' Council Res. Lab., Cincinnati, Ohio, U.S.A.). *J. Amer. Leath. Chem. Ass.*, 1956, **51** (7), 353-376.—Available methods for the determination of lignosulphonates in tanning blends have been examined and are reported. Promising results were given with Barnwell's reagent (2-naphthylamine in HCl soln.). The most reliable qualitative method was found to be the Gerngross modification of the Procter - Hirst reaction in which a filtered aq. soln. of extract is mixed with aniline and conc. HCl, shaken, and set aside; lignosulphonate forms a ppt. in 2 to 5 min. Lignosulphonates may be estimated quantitatively by pptn. with cinchonine in the presence of tannic acid and HCl at 70°.
B. R. HAZEL

See also Abstracts 1188, 1204.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

1294. Flame spectrophotometry and determination of sodium, potassium, calcium and magnesium ions in plasma and tissues. R. Valencia (Inst. de Biol. Phys.-Chim., 13 rue Pierre Curie, Paris, France). *Bull. Soc. Chim. Biol.*, 1956, **38** (7-8), 1071-1081.—The influence of the presence of the other ions and P in their usual concn. in plasma and tissue on the intensities of the emissions of Na (589 m μ), K (766 m μ), Ca (preferably 554 m μ , but also 422.7 m μ) and Mg (371 m μ) was investigated, and it is shown that for plasma the amount of Na may be determined with standards containing only Na. Phosphorus and Mg are determined colorimetrically. Potassium can then be determined by using a standard with the determined amounts of Na and P included, and Ca by using a standard with the determined amounts of the other ions. In tissue determinations, the K and the Na may each (separately) be determined by using a standard containing no other cations. The errors do not exceed $\pm 5\%$, even for Ca and Mg. Other less precise corrections are considered and rejected.
E. J. H. BIRCH

1295. Spectrophotometric titration of spinal-fluid calcium and magnesium. B. Zak, W. M. Hindman and E. S. Baginski (Detroit Receiving Hosp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1661-1665.—A sample of 2 ml is used, Ca being determined on the ptdt. oxalate and Mg on the supernatant liquid by titration with EDTA (disodium salt), with Eriochrome black T as indicator, until the steeply ascending part of the absorption curve at 660 m μ levels off. The end-point is the intersection of the extrapolated ascending and level portions of the curve. The effect of concn. of indicator and of wavelength of absorption is investigated. The method is investigated over the

desired range of Ca from 1.25 to 5 mill-equiv. per litre and Mg from 1.05 to 4.2 mill-equiv. per litre.
E. J. H. BIRCH

1296. Micro-determination of phosphorus. P. S. Chen, jun., T. Y. Toribara and H. Warner (Sch. of Med. and Dentistry, Univ. of Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1756-1758.—The sample (urine, blood product or aq. soln. of biological material after wet-ashing with H₂SO₄-HNO₃-HClO₄) containing $> 8 \mu\text{g}$ of P is adjusted to 4 ml and to this is added a reagent containing ammonium molybdate and ascorbic acid in dil. H₂SO₄. After incubation at 37° for 2 hr., the absorption is measured at 820 m μ against a reagent blank. Conditions affecting the colour production are examined, and the results compared with those of other procedures. A precision of $\pm 2\%$ and a sensitivity of 0.15 μg are quoted.
D. A. PANTONY

1297. Method for determination of arsenic in bone by radio-activation. M. E. Kohn-Abrest. *Ann. Falsif.*, 1956, **49**, 407-408.—Experimental details and calculations for a method described by Michon (*Anal. Abstr.*, 1957, **4**, 610) are given. A portion of the bone sample (0.75 g), previously dried over conc. H₂SO₄ in a vacuum, is irradiated in an atomic pile (Saclay) for 8 hr. The organic matter in the sample is destroyed by the method of Pien (*Anal. Abstr.*, 1955, **2**, 504). A known wt. of arsenous acid (not irradiated) is added to the digest and the mixture is dispersed in conc. HCl (16 ml). The arsenic is separated by distillation in the presence of cuprous chloride. Sodium hypophosphate soln. is added to the condensate and the ptdt. arsenic is filtered off, washed, dried and weighed. A known proportion of the arsenic is recovered by this means and its activity is measured in a Geiger counter. By comparison of the result with that given by irradiated pure arsenous acid, the amount of arsenic in the original sample can be calculated.
D. G. FORBES

1298. The detection of glutethimide (Doriden) and a metabolite in dog urine. H. Sheppard, B. S. D'Asaro and A. J. Plummer (Res. Dept., Ciba Pharmaceutical Products Inc., Summit, N.J.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (10), 681-684.—A method of analysis is described for glutethimide (α -ethyl- α -phenylglutarimide) (**I**) and its metabolite, α -phenylglutarimide (**II**), and a conjugated form of **II**. The method is applicable to the analysis of samples of urine and (with slight modification) blood. It is based on the formation of a hydroxamic acid derivative which gives a purple complex with Fe³⁺. **I** and **II** can be distinguished by chromatography on paper with light petroleum-methanol (1:1) as mobile phase; the *R_F* values are 0.83 for **I** and 0.67 for **II**. *Procedure*—For **I** and **II**, extract the urine (25 ml) with benzene (25 + 15 ml), evaporate the combined extracts in a vacuum to about 5 ml, dry with Na₂SO₄ and apply to a column of dried Al₂O₃ (1 g). Wash with benzene (25 ml) and elute with a dry mixture of CHCl₃-methanol (9:1). Evaporate the first 25 ml of eluate to dryness, dissolve the residue in methanol (1 ml), add 2 M hydroxylamine hydrochloride soln. (1 ml) and 3.5 N NaOH (1 ml), mix, and allow to stand at room temp. After 30 min., add 3.5 N HCl (1 ml) and 0.37 M FeCl₃ in 0.1 N HCl soln. (1 ml); mix, and measure the extinction against a reagent blank in a Klett - Summerson colorimeter with filter No. 54. For the conjugated form of **II**, add conc. HCl (3.6 ml) to the urine after extraction

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of **I** and **II**, reflux for 6 hr., cool, extract with benzene and proceed as above, but with 5 g of Al_2O_3 .

A. R. ROGERS

1299. Semi-quantitative specific test paper for glucose in urine. J. P. Comer (Anal. Res. Dept., Eli Lilly and Co., Indianapolis, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1748-1750.—The method depends on the use of test papers on which specific oxidation of the glucose to gluconic acid and H_2O_2 by glucose oxidase, followed by the formation of a blue colour with *o*-tolidine and H_2O_2 catalysed by horseradish peroxidase, occurs. The surprising temperature-independence of the method is attributed to competition for the H_2O_2 by catalase, present as an impurity. Many drugs present in the urine are shown not to interfere. The reliability of the test with various observers is investigated. The paper is stable for six months at 50° if protected from the light. The pH of the urine does not affect the test.

E. J. H. BIRCH

1300. Colorimetric determination of heptuloses. J. Šonka and M. Kuchařová (Biochem. Lab., III Int. Hospital, Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (3), 388-390.—Heptulose reacts with orcinol, dissolved in trichloroacetic acid and butanol, to give a coloration that has an absorption maximum at 600 m μ . This reaction was used for the determination of heptuloses in blood, blood serum and erythrocytes (in concn. of 1 mg-%), but not in urine. *Procedure*—Mix 3 ml of reagent with 2 ml of deproteinated sample, and heat in a closed test-tube (2 cm \times 16 cm) for 1 hr. on a boiling-water bath; cool, and measure the extinction at 620 m μ . *Reagent*—Dissolve trichloroacetic acid (80 g) in water, add orcinol (0.5 g) and dilute to 100 ml. If stored in a cool place in the dark the reagent is stable for a week.

J. ZÝKA

1301. A simple microcolorimetric method for the determination of pyruvate in 0.1-ml samples of blood. G. Rindi and G. Ferrari (Inst. Human Physiology, Univ. of Pavia, Italy). *Experientia*, 1956, **12** (10), 398-399.—Blood (0.1 ml) after haemolysis is pptd. with trichloroacetic acid soln. After removal of the ppt. by centrifuging and washing, the mixed supernatant liquid and washings along with a reagent blank are placed in a water bath at 25°. After 5 min., 0.2 ml of 0.25% (w/w) 2:4-dinitrophenylhydrazine in 2 N HCl is added to each tube, and the reaction is allowed to proceed for exactly 5 min.; 2 ml of water-saturated toluene is added to each tube removed from the bath and both tubes are vigorously shaken for 90 sec., then centrifuged for 5 min. at 3500 r.p.m. The aq. layer is discarded and the toluene layer is extracted with 3 ml of Na_2CO_3 soln. [10% (w/v)] by vigorously shaking for 90 sec. After 5 min. centrifugation, 1 ml of 1.2 N NaOH soln. is added to a 2-ml aliquot of the carbonate layer. The extinction of the reagent blank and the sample is read after 15 min. in a Beckman D.U. spectrophotometer at 445 m μ against a water blank in a 1-cm cuvette. The colour is standardised against Na pyruvate.

R. S. TONKS

1302. Two-dimensional paper chromatography of urinary indoles and related substances. C. E. Dalglish (Postgraduate Med. Sch., Ducane Rd., London). *Biochem. J.*, 1956, **64** (3), 481-485.—Indoles and other tryptophan metabolites are separated on two-dimensional paper chromatograms with the org. layer of a mixture of butanol - acetic acid - water (4:1:5, by vol.) as the first solvent and

20% (w/v) aqueous KCl as the second solvent. The chromatographic behaviour of nearly 50 indoles, tryptophan metabolites and related compounds is described, and the chromatographic pattern of the main substances related to tryptophan metabolism is summarised in a "map of the spots."

J. N. ASHLEY

1303. Determination of small quantities of histamine in the presence of much histidine. A. [Mrs. M.] Bodászky, J. Hollós and A. [Mrs. O.] Németh (Res. Inst. Pharm. Ind., Újpest, Hungary). *Magyar Kém. Foly.*, 1956, **62** (9), 317-318.—Dissolve histidine hydrochloride (1 g) in warm water (4 ml), add 96% ethanol (60 ml), cool and filter. Wash the ppt. with ethanol (2×5 ml) and evaporate the alcoholic filtrate to dryness *in vacuo* at $\approx 60^\circ$. Suspend the residue in ethanol (20 ml), filter and concentrate the filtrate to a vol. of 0.5 to 1 ml and add 0.1 N NaOH (0.1 ml). Use this soln. to moisten repeatedly a pentagonal piece (≈ 5 sq. cm) of Macherey Nagel 661 filter-paper, drying the paper between each moistening. Sew the dry paper on to Macherey Nagel 214 paper. As solvent use ethanol - *n*-butanol - H_2O (1:4:5) for 40 hr., by the descending method. Dry the paper in warm air, spray it with ethanolic ninhydrin (0.2%), dry it again in warm air, and finally at 110° for 10 min. The violet spot of histidine hydrochloride and the pink spot due to histamine can be distinguished. Known mixtures are used as control; from the size of the spots and the intensity of their colour, an approximate quant. estimate can be obtained. The sensitivity is 10 to 20 μg per gram; other, histamine-like, impurities can also be detected. A. G. PETO

1304. Micro-determination of histamine in protein hydrolysate. S. K. Dutta (Bengal Immunity Res. Inst., Calcutta, India). *Sci. & Cult.*, 1956, **21** (10), 610-611.—Histamine, together with some diazotisable substances, other than amino acids, can be separated from the bulk of a preparation by an ion-exchange resin [Zeo-Karb 226 (Na form)], leaving unadsorbed amino acids and peptides; the histamine is then quant. eluted with *N* HCl; conversely, De-Acidle FF (K form) was successfully used to adsorb amino acids and peptides, leaving histamine bodies in the colourless eluate. The histamine bodies with some other diazotisable substances thus separated were then further freed from salts and any fluorescent materials. The final soln. of histamine and other bodies was chromatographed on specially washed Whatman No. 1 paper with a solvent mixture of *n*-butanol, isopropyl alcohol and aq. NH_3 (10:15:5) in an atmosphere of ammoniacal butanol. Histamine gave an R_F of 0.5 and the other diazotisable substances an R_F of 0.75. The spot parallel to that from standard histamine was cut out, eluted with 0.1 N HCl at about 60° to 70° and analysed for total histamine by Pauly's method (at 500 m μ) and for total N by the micro-Kjeldahl method. As little as 0.2 μg of histamine per ml of the protein hydrolysate could be correctly determined in this way. P. HAAS

1305. Colorimetric method for determination of glucosamine and galactosamine. S. Roseman and I. Daffner (Dept. of Biol. Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1743-1746.—Glucosamine and galactosamine give equivalent extinctions when determined colorimetrically by the Elson - Morgan procedure (acetylacetone - Ehrlich reagent), but by an acetic anhydride procedure, in which the acetylated com-

pounds are treated first with alkali and then with Ehrlich reagent, the galactosamine must be present in a concn. of about four times that of the glucosamine to give the same extinction, so that by the use of both methods, which are described in detail, the quantity of each hexosamine present may be calculated. The error found for unhydrolysed mixtures can be as much as 9.1% and for hydrolysed samples 11%. The method is applied to various compounds of biological origin which give rise to these amino sugars on hydrolysis.

E. J. H. BIRCH

1306. Colorimetric determination of two azotiodothyronines in different media. G. Barac and O. Quadens (Inst. de Clinique et de Polyclinique Med., Univ. de Liège, Belgium). *Bull. Soc. Chim. Biol.*, 1956, **38** (7-8), 1055-1062.—Two 25-mg samples, one of 3:5:3'-tri-iodo-5'-(4-sulphophenylazo)thyronine and one of 5'-(4-arsenophenylazo)-3:5:3'-tri-iodothyronine, are treated with 0.5 ml of N NaOH and made up to 500 ml. These soln. have extended absorption max. in the region of S_{47} to S_{55} of the Pulfrich photometer and obey Beer's law. Beer's law is also obeyed by these tri-iodothyronines in plasma and in urine, but with different absorptions. It was found that proteins do not affect the absorption, but that pH does. The photometric results for these tri-iodothyronines in urine and in plasma at pH 5.8 and 7.4, respectively, are in good accord with the results for pure soln. E. J. H. BIRCH

1307. Quantitative paper chromatography of lipids. J. L. Gellerman and H. Schlenk (Hormel Inst., Univ. of Minnesota, Austin, U.S.A.). *Experientia*, 1956, **12** (9), 342-343.—Mixtures of fatty acids of the C_{18} series, their methyl esters and the unsaturated mono-acid triglycerides have been analysed. Whatman No. 1 paper treated with Dow Corning 200 fluid was used in ascending chromatographic technique. Chromatograms of fatty acids or esters were developed for 16 to 20 hr. at $30^\circ \pm 1^\circ$ with a mixture of aq. formic acid (88%) and acetic acid (85%) (1:1 by vol.), and the triglycerides were separated at $24^\circ \pm 1^\circ$ with $CHCl_3$ -methanol (3:1 by vol.). A densitometer was used for measuring the extinctions of brown spots in blue light (filter 445 m μ), and for the transmission of white spots on purple background in green light (filter 525 m μ). R. S. TONKS

1308. Quantitative analysis of amino acids using paper chromatography. R. H. Hackman and M. Lazarus (Div. of Entomology, C.S.I.R.O., Canberra, Australia). *Aust. J. Biol. Sci.*, 1956, **9** (2), 281-292.—A simple method for the quant. analysis of amino acids in a protein hydrolysate or other mixture of amino acids is described. The amino acids are separated on one-dimensional paper chromatograms, four solvent systems being used to resolve 17 amino acids. The chromatograms are treated with a suitable reagent to detect the spots corresponding to each amino acid. Each chromatogram, after being made semi-transparent with dimethyl phthalate, is scanned automatically with a densitometer, and the intensity of the light transmitted by the coloured spots is recorded on light-sensitive paper. A rectilinear relationship between concn. and log per cent. transmission was found to hold for all the amino acids. The most useful range of amino-acid concn. was 2 to 5 mM, although the method is usable in the range of 1 to 10 mM. The method contains several new techniques and the average coeff. of variation for a single reading for an amino acid is 5.7%. P. HAAS

1309. Rapid procedure for estimation of amino acids by direct photometry on filter-paper chromatograms. Estimation of seven free amino-acids in orange juice. L. B. Rockland and J. C. Underwood (Agric. Res. Service, U.S. Dept. of Agric., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1679-1684.—The amino acids in orange juice from two varieties of orange are chromatographed on strips of S. & S. No. 507 paper (2.7 cm \times 21.5 cm); various solvents are used in a tank adapted to take 40 strips simultaneously. A solvent comprising 2:4:6-collidine - 2:4-lutidine - water (100:100:92.3) separates arginine from major nitrogenous constituents; one of phenol - aq. NH_3 - water (*Anal. Abstr.*, 1955, **2**, 273) separates aspartic acid, glutamic acid, serine and alanine, and one of *tert*.butyl alcohol-formic acid - water (69.5:1.0:29.5) separates γ -aminobutyric acid and proline from the other constituents, but not from each other. Staining is usually carried out with ninhydrin, with which the yellow colour given by proline does not interfere. Proline is determined by the blue colour produced with isatin. Procedures are detailed for the preparation of the chromatograms and for the measurement of the intensity of the spots with an adapter (described) for the Lumetron photometer. The assay range is from 0.1 to 1.0 μ g.

E. J. H. BIRCH

1310. Colorimetric micro-determination of tyrosine. C. Dumazert, C. Ghiglione and M. Bozzitachaudou (Lab. de Chim. de la Fac. de Méd. et de Pharm., 92 rue A. Blanqui, Marseille, France). *Bull. Soc. Chim. Biol.*, 1956, **38** (7-8), 1083-1088.—2:4:6-Tribromophenylidiazonium reagent is made by dissolving 200 mg of tribromoaniline in 2 ml of conc. H_2SO_4 , treating the soln. with 50 mg of $NaNO_2$ in 2 ml of conc. H_2SO_4 (the acid is added rapidly to the nitrite), pouring the mixture into 60 ml of ice water and making up to 100 ml. It can be kept for several hours at 4° . To a 5-ml sample containing tyrosine (30 to 160 μ g) is added 1 ml of the reagent, and after being shaken and set aside for 5 min. the mixture is made up to 10 ml with 20% Na_2CO_3 . By heating for 35 min. on the water bath, a pink colour is developed, which is thought to be due to the formation of 9-(2-amino-2-carboxyethyl)-1:2:7:8-di(3:5-dibromobenzene)-10-hydroxy-3:4:5:6-tetra-aza-anthracene, and is measured at 525 m μ against a blank. Tyrosine is separated from interfering amino acids in protein hydrolysates by the technique of Fromageot *et al.* (*Brit. Abstr. C*, 1950, 182) and can be determined. Results obtained agree with those of Lugg's method within $\pm 2\%$.

E. J. H. BIRCH

1311. The metabolism of tryptophan. II. The metabolism of tryptophan in patients suffering from cancer of the bladder. [Determination of tryptophan metabolites.] E. Boyland and D. C. Williams (Chester Beatty Res. Inst., Fulham Rd., London). *Biochem. J.*, 1956, **64** (3), 578-582.—Anthranilic acid, 3-hydroxyanthranilic acid and its sulphuric ester, kynurenone, 3-hydroxykynurenone and its sulphuric ester are quantitatively removed from urine by deactivated charcoal, and these six tryptophan metabolites are separated by chromatography by using a gradient-elution partition system. They are determined spectrophotometrically in the eluates, kynurenone and its derivatives at 365 m μ , and anthranilic acid and its derivatives at 330 m μ .

J. N. ASHLEY

1312. The photometric determination of small quantities of ergothioneine. A. Kornhauser and M. Perpar (Inst. of Organ. Chem., Univ. Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1956, **153** (4), 268-270.—The absorption curve of ergothioneine in water is given. Maximum absorbancy is at 257 m μ ($E_{1\text{cm}}^{1\%} = 546$), and Beer's law is obeyed for concn. of 0.003 to 0.03 mg of ergothioneine per ml. It is said to be possible to estimate the ergothioneine of single sclerotia of ergot, but no details of the extraction procedure are given. P. S. STROSS

1313. The decolorisation of paper-electrophoresis strips. A practical apparatus. M. Girard and F. Rousselet (Lab. Central de Chim. Biol. Pharm. de l'Hôpital Lariboisière, Paris, France). *Bull. Soc. Chim. Biol.*, 1956, **38** (7-8), 1089-1095.—An apparatus is described for the removal of excess of dyestuff (Amido black 10 B) from the paper-electrophoresis strips that have been used for the separation of proteins. The dried paper, treated with the dyestuff, is put into a tube filled with methanol-acetic acid (9:1) (the acetic acid stabilises the protein-dye complex). This tube is fed with methanol from a reflux condenser while the continuous (unsiphoned) overflow passes to a round-bottomed flask whence it is distilled into the condenser. The results and advantages of the method are discussed. E. J. H. BIRCH

1314. Rapid determination of radiocarbon in animal tissues. E. M. Pearce, F. DeVenuto, W. M. Fitch, H. F. Firschein and U. Westphal (Army Med. Res. Lab., Fort Knox, Ky., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1762-1765.—A method of dissolving dried tissues and organs containing [^{14}C]cortisol {[^{14}C]17-hydroxycorticosterone} in hot formamide and measuring the radioactivity after drying an aliquot on filter-paper in a planchette is described. E. G. CUMMINS

1315. A light source for locating oestrogens on chromatograms. D. D. Perrin (Ruakura Animal Res. Sta., Hamilton, New Zealand). *Nature*, 1956, **178**, 1244.—A magnesium spark emits most of its photographically active radiation between 2791 and 2803 Å and is therefore very suitable for detecting oestrogens (absorption max. about 280 m μ) on paper chromatograms. A 15-kV spark system assembled from readily available components enables 1 μg of oestrone per sq. cm to be detected photographically. The photographs are taken through Whatman No. 1 filter-paper in contact with Ilford reflex document paper, with a 10-sec. exposure at 70 cm. The spark system described can be run in air for periods up to 1 min. without the electrodes igniting. K. A. PROCTOR

See also Abstracts 1118, 1333, 1347, 1383.

Drugs

1316. High-frequency titrations in pharmaceutical analysis. J. Allen, E. T. Geddes and R. E. Stuckey (British Drug Houses Ltd., London). *J. Pharm. Pharmacol.*, 1956, **8** (11), 956-966.—Reference is made to three methods of measuring the electrical changes at the end-point, *viz.* the tuned-anode-tuned-grid oscillator method (*cf.* Lane, *Anal. Abstr.*, 1956, **3**, 453), the rectified radio-frequency impedance method (*cf.* Blake, *Analyst*, 1950, **75**, 32), and the Q-meter (*cf.* Blake, *J. Sci. Instrum.*, 1945, **22**, 174); band or coil electrodes can be used. The Q-meter is most generally applicable. The method

is shown to give results comparable with those of the official assays for acid-base and pptn. titrations in aq. soln. and for the non-aq. titration of sulphonamides and the sodium or potassium salts of organic acids.

A. R. ROGERS

1317. Method for the quantitative determination of alkaloidal salts by cation exchange and subsequent compleximetric titration. E. Sjöström and W. Rittner (Arzneimittelfabrik Orion Oy, Helsinki, Finland). *Z. anal. Chem.*, 1956, **153** (5), 321-324.—A method is described for the quantitative estimation of alkaloidal salts, *e.g.*, cocaine hydrochloride, in aqueous solution by cation exchange with Mg²⁺. The Mg²⁺ are titrated with EDTA, with Eriochrome black T as indicator. The method is rapid and 15 to 100 mg of alkaloidal salt can be determined with a mean error of approximately $\pm 0.25\%$.

M. F. C. LADD

1318. Microchemical studies on plant components. XXII. Separation and detection of morphine-type alkaloids by paper chromatography and paper electrophoresis. Tatsuo Kariyone and Takao Inoue (Pharm. Inst., Med. Faculty, Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1956, **76** (6), 625-628.—Paper-chromatographic detection of morphine (**I**), ethylmorphine (**II**), diamorphine (**III**), codeine (**IV**) and hydrocodeine (**V**) was studied by the method of McFarren (*Anal. Chem.*, 1951, **23**, 172). The paper is impregnated with a buffer soln. of various pH values (1 to 12) and developed with butanol saturated with the same buffer. The separation of spots of **II** and **III** (pH 12) and of **IV** and **V** (pH 9 to 11), which is otherwise difficult, can be achieved. The spots are detected with iodine vapour, Dragendorff's reagent or a mixture of chloroplatinic acid and KI. Their separation was also attempted by paper electrophoresis (500 V, 0.5 to 2.0 mA per cm, 4.5 hr.) in aq. NH₃ soln. of various concn. (0.01 to 1%). In 0.5 or 1% aq. NH₃ soln. they are classified into two groups, **I** and **III**, and **II**, **IV** and **V**.

XXIII. Separation of xanthine derivatives by paper chromatography. Takao Inoue. *Ibid.*, 1956, **76** (6), 629-631.—Paper-chromatographic separation of caffeine (**VI**), theophylline (**VII**), theobromine (**VIII**), 3-methylxanthine (**IX**) and xanthine (**X**) was studied with various developing agents. Butanol saturated with 0.1% aq. NH₃ soln. and a mixture of isoamyl alcohol and 0.1% aq. NH₃ soln. (7 + 1) are the best. The *R_F* values (0.70, 0.55, 0.41, 0.21 and 0.14 for **VI**, **VII**, **VIII**, **IX** and **X**, respectively, with the former developer) increase with increase in the number of CH₃ groups. When development is with butanol saturated with Sørensen's buffer of various pH values (1.2 to 12.7) by the buffer chromatography, the separation of **VII** and **VIII** is effected at pH 3 to 8. Circular paper chromatography is also satisfactorily applied by the use of the developers mentioned above. The spots are detected by illuminating with u.v. light of 240 to 270 m μ (limit of detection, 0.5 μg for **VI**, **VII** and **VIII**; 0.1 μg for **IX** and **X**). These methods are used for the detection of these alkaloids in tea, cacao, coffee and guarana.

XXIV. Separation of xanthine derivatives by paper electrophoresis. Tatsuo Kariyone and Takao Inoue. *Ibid.*, 1956, **76** (6), 747-748.—By paper electrophoresis (500 V, 3 hr.) at pH > 8.5, **VII**, **IX** and **X** migrate towards the anode, the rate increasing with increase in pH, whereas **VI** and **VIII** migrate towards the cathode. The separation of the spots of **VII** and **VIII** and those of **IX** and

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[Abstr. 1319–1326]

X is satisfactorily effected in 0·5% borax soln. Other ingredients in the sample (tannins, flavones, etc.) migrate towards the anode and do not interfere with the detection.

K. SAITO

1319. The evaluation of belladonna herb. I. The quantitative determination of seed in powdered herb. R. G. Atkinson and C. Melville (Pharm. Dept., Univ. Manchester, England). *J. Pharm. Pharmacol.*, 1956, **8** (11), 927–936.—A projection method for the determination of the surface area of objects of irregular shape is applied to the measurement of the surface area of belladonna seeds. By combining the results with counts of the testa cells per unit surface area, the number of testa cells per unit wt. of seed has been calculated. The figures agree with those obtained by lycopodium counts. A method involving acid maceration under carefully controlled conditions of time and temp. is described for the separation of testa cells of belladonna seed from other cellulose material in the powdered herb. This enables a quant. estimate to be made of the amount of seed present in the powdered herb.

A. R. ROGERS

1320. A method of determining binary mixtures by distribution measurements, and its application to the assay of strychnine in the presence of quinine. C. Morton and E. H. Tinley (School of Pharm., Chelsea Polytechnic, London). *J. Pharm. Pharmacol.*, 1956, **8** (11), 967–974.—When a mixture of two substances is dissolved in a suitable solvent and shaken with an immiscible solvent, the wt. of mixed solutes present in each phase at equilibrium is a function of the composition of the original mixture. If, after separation of the phases, the weight of mixed solutes in either phase is determined, the relative proportions of the components in the mixture may be read on a calibration graph constructed empirically from data obtained with mixtures of known composition. The method is exemplified by the assay of strychnine in the presence of quinine, for which the graph is linear. *Procedure*—Dissolve the mixture ($\approx 0\cdot4$ g) in *N* HCl (20 ml) and shake for 1 hr. at 25° with CHCl_3 (50 ml). Separate the organic phase, filter through dry paper, evaporate a 40-ml aliquot to dryness and dry to constant wt. at 105° . The percentage of strychnine = $215w - 1\cdot0$, where w is the wt. of residue from 1 g of mixture.

A. R. ROGERS

1321. Simple estimation of alkaloids in ephedra by circular paper chromatography. Takeshi Shimano, Mizuo Mizuno and Shin-Ichiro Yamato (Gifu College of Pharmacy, Kokonoe-cho, Gifu). *J. Pharm. Soc. Japan*, 1956, **76** (7), 860–861.—Circular paper chromatography was applied to the determination of ephedrine (**I**) in ephedra. The sample (2 g) is extracted with methanol (20 ml) and the soln. (evaporated to 2 ml) is spotted on to the centre of a circular filter-paper, developed with butanol saturated with water for 50 to 90 min., dried and revealed by keeping the paper in iodine vapour for 2 to 3 hr. The area of the light-brown spot is proportional to the log. of the concn. of **I** ($<1\cdot0 \mu\text{g}$ per drop). The result compares well with that obtained by the titration method.

K. SAITO

1322. The detection of hydrolysis products in reserpine. M. Langejan and H. F. L. Liefferink (Farm. Lab., Rijksuniv., Utrecht, Holland). *Pharm. Weekbl.*, 1956, **91** (23), 847–854.—By alkaline hydrolysis of reserpine, degradation products are formed which interfere with the fluorimetric determination of reserpine. A chromatographic method is des-

cribed in which Whatman No. 1 paper is used, with a mixture of butanol, butyl acetate, water and glacial acetic acid (9:4:16:28) as an ascending solvent. After 18 hr., the paper is air-dried and examined in u.v. light. R_F values for reserpine and two of its hydrolysis products were found to be 0·97, 0·84 and 0·56 to 0·62, respectively.

P. HAAS

1323. Determination of total alkaloids in rauwolfia root. F. Neuwald and W. Loges (Priv. Apoth. Schönberg, Holstein, Germany). *Arch. Pharm., Berlin*, 1956, **289** (4), 226–231.—Comparative assays by the B.P.C. 1954 method, the "rapid extraction" method (Hörhammer and Rao, *Anal. Abstr.*, 1954, **1**, 1340), and the method of Eder (*Pharmazie*, 1955, **10**, 236) gave similar results, but the pharmacological activities of the extracted material when assessed on the blood pressure of a cat varied widely, only the last method showing high activity.

G. R. WHALLEY

1324. The assay of *Rauwolfia serpentina* preparations. D. Banes, J. Wolff, H. O. Fallscheer and J. Carol (Div. Pharm. Chem., Food and Drug Admin., Washington, D.C.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (10), 708–709.—A method is described for the absorptiometric analysis of *Rauwolfia serpentina* root and preparations, based on reaction between the reserpine-rescinnamine group of alkaloids and HNO_2 . The results agree well with those obtained by chromatographic analysis (*cf. Anal. Abstr.*, 1956, **3**, 2847). *Procedure*—Extract the sample (2 or 3 g) with ethanol (100 ml) in a Soxhlet apparatus. Dilute the extract to 100 ml, mix a 20-ml aliquot with 0·5 N H_2SO_4 (200 ml), and extract with trichloroethane (3 \times 25 ml); wash each extract with 0·5 N H_2SO_4 (50 ml) and discard. Extract the aq. soln. with CHCl_3 (85 ml in six portions); wash each extract with the same 0·5 N H_2SO_4 (50 ml) and 2% aq. NaHCO_3 (2 \times 10 ml). Add the combined CHCl_3 extracts to ethanol (10 ml) and dilute to 100 ml. Mix a 10-ml aliquot with ethanol (4 ml), evaporate at a temp. $< 70^\circ$ and dry in a vacuum desiccator. Dissolve the residue in ethanol (5 ml), add 0·5 N H_2SO_4 (1 ml) and 0·3% aq. NaNO_2 (1 ml), mix, warm at 50° to 60° for 20 min., cool, add freshly prepared 5% aq. sulphamic acid, mix, and determine the extinction at 390 m μ in a 1-cm cell against 67% ethanol. Compare the extinction with that of blank and standard soln.

A. R. ROGERS

1325. Colorimetric determination of digitalis glycosides with methyl 3:5-dinitrobenzoate. D. H. E. Tattje (Lab. v. Farmacog., Rijksuniv., Groningen, Holland). *Pharm. Weekbl.*, 1956, **91** (23), 841–846.—The glycoside, dissolved in 4 ml of methanol, is mixed with 5 ml of a 1·5% (w/v) soln. of methyl 3:5-dinitrobenzoate in methanol. After the addition of 1 ml of 0·45 N NaOH, the colour is measured at 535 m μ in a 1-cm cell against a blank. The mol. extinctions of digitoxin, digoxigenin and gitoxigenin are 10,100, 10,300 and 7600, respectively. By boiling with acid (*cf. Ibid.*, 1956, **91**, 541) the mol. extinctions of digoxigenin and gitoxigenin are increased to 12,800 and 8300.

P. HAAS

1326. The polarographic determination of santonin. Tatsumi Suzuki and Masahidi Ito (Depart. of Chem., Mie Prefectural Univ., Tsu, Japan). *Mie Med. J.*, 1956, **6** (1–2), 105–111 (in English).—A simple polarographic method has been established for the determination of santonin in the leaves and flower-heads of *Artemisia kurramensis* Qazilbash.

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The santonin is obtained by Soxhlet extraction with CHCl_3 followed by evaporation and dissolution in purified ethanol. An aliquot is taken and ethanol is added to a concn. of $> 25\%$ to prevent crystallisation, followed by 1 ml of $N \text{ KCl}$, and the soln. is made up to 10 ml with buffer (pH 3-0) (0-2 M citric acid - 0-2 M sodium dihydrogen phosphate). The polarogram is recorded from 0-5 to 1-5 V. A calibration curve is made from dilutions ($0-5 \times 10^{-3} M$ to $3-5 \times 10^{-3} M$) of the standard solution [$0-4924\%$ (w/v)] and this is compared with polarograms recorded from the sample solution and a mixture of sample and pure solution of santonin of various concn. The error of the method decreases with increase of santonin present.

D. P. FELIX

1327. Determination of riboflavin in pharmaceutical products. L. Brealey and D. A. Elvidge (Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1956, **8** (11), 885-893.—Riboflavin (**I**) can be determined by direct spectrophotometry in a buffer of pH 4-0; $E_{1\text{cm}}^{1\%}$ (445 m μ) = 308. Alternatively, the change in extinction on addition of dithionite and reoxidation can be measured; $\Delta E_{1\text{cm}}^{1\%}$ (445 m μ) = 264. In many cases when artificial colouring matter is present, this is reduced by dithionite but not reoxidised by aeration, and so does not interfere. The method has been applied successfully to the assay of tablets, capsules and liquid multivitamin preparations. It is less sensitive than the fluorimetric procedure, but is more specific and flexible. *Procedure*—Prepare a soln. of the sample (containing 0-2 to 0-4 mg of **I**) in phosphate buffer of pH 4-0 (20 ml). Add 5% aq. sodium dithionite (0-1 ml) and measure the extinction at 445 m μ after 1 min. Aerate the soln. for 1 min. and remeasure the extinction at 445 m μ .

A. R. ROGERS

1328. Quantitative determination of Syntomycin [DL-chloramphenicol] and Laevomycetin [chloramphenicol] in pharmaceutical preparations and mixtures. G. A. Vaisman and M. D. Kislaya (Kiev Post-graduate Medical Inst.). *Apteknoe Delo*, 1956, **5** (4), 19-22.—Syntomycin (or Laevomycetin) is reduced with Zn and dil. H_2SO_4 and the chloride formed is determined argentimetrically. *Procedure*—A weighed sample (0-1 to 0-15 g) is treated with 10 to 15 ml of dil. H_2SO_4 and 1 g of zinc dust in a 100-ml flask fitted with a reflux condenser. The flask is set aside at room temp. for 5 min. and it is then heated on a bath of boiling water for 10 min. The flask is cooled, 10 to 15 ml of water is added through the condenser and the contents are filtered. To the filtrate and washings are added 10 ml of 0-1 N AgNO_3 , 5 ml of dil. HNO_3 and 2 to 3 ml of ferric ammonium sulphate soln., and the excess of AgNO_3 is titrated against 0-1 N NH_4SCN . Results are satisfactory with preparations containing calcium carbonate, bismuth subnitrate, phenolphthalein, dextrose, soft paraffin wax or fats. The precision is $\pm 3\%$.

E. HAYES

1329. Identification reactions of the three tetracyclines. M. A. Fouchet (École de Méd. et Pharm., Angers, France). *Ann. Pharm. Franç.*, 1956, **14** (4), 281-284.—*Procedure*—An aq. solution of ZnCl_2 (50%) (2 ml) is heated until it forms a skin and is then heated for 1 min. with a trace of the substance to be identified. The residue is dissolved in dil. acetic acid. Chlortetracycline gives a garnet-red residue dissolving to dichromate yellow in the acetic acid solution, tetracycline gives a yellow residue dissolving to a chromate yellow, and oxy-

tetracycline an amethyst-coloured residue. Use of a stronger acid (pH < 1-5) causes formation of a rust-coloured ppt.

E. J. H. BIRCH

1330. Determination of neomycins B and C in neomycin sulphate. A. A. Brooks, A. A. Forist and B. F. Loehr (Res. Lab., The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1788-1790.—The difference in optical rotation of neomycins B and C and the production of furfuraldehyde on acid treatment (measured absorptiometrically) is used as a composite method for their determination. A second method comprises measurement of the variation of optical rotation with temp.; and a third method makes use of optical rotation and the neutralisation equivalent. Of these procedures, the first is preferred. The error for total neomycin is $\approx \pm 1\%$, for neomycin B, $\pm 3\%$, and for neomycin C, $\pm 10\%$.

E. J. H. BIRCH

1331. Polarographic analyses of mixtures of prednisone and cortisone. P. Kabasakalian, S. DeLorenzo and J. McGlotton (Res. Div., Schering Corp., Bloomfield, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1669-1670.—Although the polarographic waves of prednisone ($E_\frac{1}{2} = -1.20$ V vs. the S.C.E.) and cortisone ($E_\frac{1}{2} = -1.36$ V) encroach slightly when measured in 50% methanol buffered to pH 5-5 with Na acetate-acetic acid, they can be determined by current measurements at -0.90 V (zero point), -1.31 V (prednisone plateau) and -1.47 V (cortisone plateau), and by the use of the current constants ($i_{d/C}$) determined for a pure soln. of steroid whose concn. is half that of the sample assayed. The accuracy is within $\pm 4\%$ for the major and $\pm 2\%$ for the minor constituent. For more than 90% of one steroid the accuracy is increased by the use of current constants determined for such soln. The standard deviation is within $\pm 0.8\%$ for concn. ≥ 1 g per litre.

E. J. H. BIRCH

1332. Gas-chromatographic determination of some hydrocarbons in cigarette smoke. H. W. Patton and G. P. Touey (Tenn. Eastman Co., Div. of Eastman Kodak Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1685-1688.—Samples (10 ml) of cigarette smoke with liquid and solid phases filtered out are collected from 1-3 to 3-sec. puffs of 35 ml in a cigarette-smoking machine (*Anal. Chem.*, 1955, **27**, 1788), and are chromatographed on a column (130 cm \times 0.55 cm) packed with silica gel, with He at 50 ml per min. as carrier gas. The thermal conductivity of the effluent gas is continuously recorded. The results obtained, based on comparison with known mixtures, are ethane (0.2), ethylene (0.1), acetylene (0.01), propane (0.06), propylene (0.07), isobutane (0.001), and butane (0.006% by vol.). The effect of duration of puff and length of unsmoked butt is measured for three different brands. The only significant effect is an increase of ethane, ethylene, propane and propylene as the butt-length decreases.

E. J. H. BIRCH

1333. Toxicological investigation of micro quantities of barbiturates. O. A. Guagnini, E. E. Vonesch, A. M. Fassi and S. V. Guagnini (Nat. Univ. of La Plata, Buenos Aires). *An. Asoc. Quim. Argentina*, 1956, **44** (1), 44-51.—A method developed for determining micro quantities of barbiturates in physiological extracts, etc., has a sensitivity of 10 to 15 μg . Viscera are homogenised, acidified with tartaric acid and desiccated with Na_2SO_4 , and extracted continuously, first with light petroleum and then

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[Abstr. 1334-1341]

with methanol. Blood samples need not be extracted with light petroleum. Small quantities on filter-paper are extracted, after being dried, with methanol containing acetic acid or HCl; the extract is evaporated and redissolved in methanol without acid. Urine samples, acidified with tartaric acid, are extracted with ether, the extract is evaporated and the residue extracted with methanol. The methanol solutions are evaporated dropwise at the bottom of a filter-paper strip and an ascending chromatogram is prepared, with methanol as solvent. This is dried and sprayed with cobalt acetate solution; on drying and exposure to NH₃, a violet-pink zone indicates the probable presence of barbiturate.

D. LEIGHTON

1334. The volumetric determination of Analgin [sodium 2:3-dimethyl-1-phenylpyrazol-5-on-4-yl-N-methylaminomethanesulphonate]. M. E. Shub and N. A. Kobzareva (All-Union Ordzhonikidze Pharm.-chem. Res. Inst.). *Aptechnoe Delo*, 1956, **5** (4), 48-49.—Analgin can be determined iodimetrically without the use of an indicator by the following method. *Procedure*—A weighed sample (0.4 g) is dissolved in 5 to 6 ml of water in a 100- or 150-ml conical flask at a temp. $\geq 20^\circ$ and the soln. is immediately titrated against 0.1 N iodine. A pink colour is first produced and this gradually disappears when about 20 ml of iodine soln. has been added; the titration is continued until the soln. assumes a permanent yellow colour.

E. HAYES

1335. New colour reaction for phenazone. N. P. Yavorskii (Lvov Med. Inst.). *Aptechnoe Delo*, 1956, **5** (4), 40-41.—When a few crystals of phenazone are heated with 0.5 ml of a 5% ethanolic soln. of xanthhydrin and one or two drops of HCl, an intense violet-red colour is produced which is stable for several days. The sensitivity limit is 35 µg of phenazone per ml of soln. The reaction can be used to detect phenazone in the presence of amidopyrine, phenacetin, aspirin, caffeine, sodium salicylate, sodium benzoate, phenobarbitone or codeine.

E. HAYES

1336. The application of enzyme inhibition to the estimation of small quantities of drugs possessing anticholinesterase activity. The assay of injection of neostigmine methylsulphate. J. Buckles and K. Bullock (Pharm. Dept., Manchester Univ., England). *J. Pharm. Pharmacol.*, 1956, **8** (11), 946-955.—This method for the assay of injection of neostigmine methylsulphate (**I**) is based on the inhibition of the pseudocholinesterase activity of horse serum. The error is large ($> 10\%$), but can be reduced by simultaneous comparison with standard injections. *Procedure*—Mix the sample (5 ml) containing 1 µg of **I** with horse serum (1 ml), 0.2% cresol red soln. (1 ml) and H₂O (37 ml), heat to 40° and adjust the pH to 7.9. After 15 min., add 3% acetylcholine perchlorate soln. (5 ml) and readjust to pH 7.9. Maintain the pH between 7.8 and 8.0 during 15 min. by dropwise addition of 0.025 N NaOH and record the vol. of alkali used. Correct for non-enzymic hydrolysis by conducting an experiment with buffer (1 ml) instead of horse serum, and carry out a blank with H₂O (5 ml) instead of sample. The percentage inhibition is a linear function of the log concn. of **I**.

A. R. ROGERS

1337. The determination of benactyzine. J. P. Jefferies and J. I. Phillips (Glaxo Lab. Ltd., Greenford, Middlesex, England). *J. Pharm. Pharmacol.*, 1956, **8** (11), 907-914.—Benactyzine hydrochloride

(2-diethylaminoethyl benzilate hydrochloride) (**I**) can be characterised by u.v. spectroscopy and by a procedure which involves hydrolysis with conc. aq. NaOH, steam-distillation, and titration of the diethylaminoethanol with standard acid. Soln. and tablets of **I** can be determined by a spectrophotometric method in which free benzilic acid and other sources of irrelevant absorption are removed by extraction with ether from an acid soln. *Procedure*—Extract a soln. of the sample (containing ≈ 40 mg of **I**) in 0.5 N HCl (20 ml) with ether (40 and 25 ml), wash the combined extracts with 0.5 N HCl (2 × 5 ml) and add the washings to the main aq. soln. Reject the ether extracts. To the aq. soln. add NaHCO₃ (1.4 g), extract at once with ether (50, 30 and 15 ml) and wash the combined ether extracts with dil. aq. NaHCO₃ (2 × 10 ml). Filter the ether soln. through cotton wool, evaporate to dryness, dissolve the residue in cold 0.1 N ethanolic HCl (100 ml) and measure the extinction in a 1-cm cell at 258.5 m μ against a reagent blank. E_{1cm}¹ for pure **I** = 12.4.

A. R. ROGERS

1338. The determination of 5-chloro-7-iodohydroxyquinoline (Vioform) and two observations on problems of the International Pharmacopoeia. F. L. Hahn. *Pharm. Zentralh.*, 1956, **95** (8), 309-312.—A method is described for the evaluation of Cl and I in Vioform by first oxidising the iodide to iodate with KMnO₄. The iodide and chloride may then be titrated separately giving good end-points, thus eliminating former difficulties.

D. P. FELIX

1339. The quantitative determination of proguanil. M. I. Pechený. *Aptechnoe Delo*, 1956, **5** (4), 41-42.—Proguanil is determined by direct titration against Hg(NO₃)₂. *Procedure*—A weighed sample (0.3 g) of proguanil is dissolved by heating in 25 ml of water; four or five drops of conc. HNO₃ and five to seven drops of diphenylcarbazone indicator are added to the cooled soln., and the soln. is titrated against 0.1 N Hg(NO₃)₂. Results are as accurate as those obtained by the gravimetric method of the U.S.S.R. Pharmacopoeia VIII (1st Suppl., 1952). Proguanil can also be determined argentimetrically, a mixture of bromophenol blue and fluorescein being used as indicator.

E. HAYES

1340. The assay of aminoacetic acid elixir by non-aqueous titration. G. Meland and M. I. Blake (Sch. of Pharm., North Dakota Agric. Coll., Fargo, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (10), 672-674.—Aminoacetic acid elixir can be assayed by non-aqueous titration; the recovery was $99.10 \pm 0.19\%$. This compares favourably with the (U.S.) N.F. X method, involving a formol titration, for which the recovery was $99.67 \pm 1.38\%$. *Procedure*—Evaporate the sample (1 ml) to dryness at a temp. $< 80^\circ$, dissolve the residue in glacial acetic acid (50 ml) and titrate with 0.1 N HClO₄ in glacial acetic acid. Determine the end-point potentiometrically or visually (methyl violet; first green colour).

A. R. ROGERS

1341. Method for determining Nipagin [methyl p-hydroxybenzoate] and other esters of p-hydroxybenzoic acid in medicines and food products. A. L. Montes (Dept. Bromatology and Ind. Anal., Fac. Exact and Nat. Sci., Buenos Aires). *An. Asoc. Quím. Argentina*, 1956, **44**, 82-89.—The methyl p-hydroxybenzoate content (as low as 20 µg) of a 2 to 10-g sample can be determined by saponifying with N NaOH, acidifying with 5 N H₂SO₄ and extracting with ether, washing the extract with

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acid and evaporating it in the presence of 10% Na_2CO_3 soln. The extinction is measured at 600 m μ , 30 min. after the addition of the Folin-Ciocalteau reagent, and the amount of ester is obtained by using a calibration curve previously recorded with dilutions of a standard solution.

D. LEIGHTON

See also Abstracts 1149, 1289, 1351, 1368, 1384.

Food

1342. Determination of calcium and magnesium in foodstuffs. Simultaneous removal of iron and phosphate as interfering ions by ion exchange.

W. E. Schilz and G. N. Krynaud (Dept. of Inorg. and Phys. Chem., Univ. of Pretoria, Transvaal, S. Africa). *Anal. Chem.*, 1956, **28** (11), 1759-1761.

The ignited foodstuff sample is evaporated to dryness with HCl and a suitable aq. soln. of the residue is treated with dil. H_2O_2 and oxalic acid. The soln. is then passed through an ion-exchange column (Amberlite IR-112), the iron oxalato complex and phosphate being eluted with dil. oxalic acid, and, later, the Mg^{2+} and Ca^{2+} with dil. HCl. The second eluate is titrated with EDTA (disodium salt) by a standard procedure, with murexide in the presence of CN^- , OH^- and hydroxylamine hydrochloride for the determination of Ca^{2+} , and Eriochrome black T in the presence of hydroxylamine hydrochloride, CN^- and an aq. $\text{NH}_3 \cdot \text{NH}_4\text{Cl}$ buffer for Mg^{2+} . Results on several foodstuffs are compared with those of standard procedures.

D. A. PANTONY

1343. The saccharimetric analysis of honey. J. Valin (Lab. Apicole de Nice, France). *Ann. Falsif.*, 1956, **49**, 388-401.—The constituent sugars in honey can be estimated from observations of the copper-reducing power of a sample soln., and after mild and vigorous inversion. An account of the properties of a trisaccharide (melitizose) is given and the method of analysis takes advantage of the fact that this substance is unaffected by the action of saccharase, but is partially hydrolysed by the Clerget process and further by a more vigorous treatment. Saccharase is prepared from baker's yeast. The yeast (100 g) is dispersed in water (50 ml) and filtered through a Buchner funnel. Ethanol (95%) (200 ml) is added to the filtrate and the mixture is set aside overnight. The ethanol is decanted and the residue is filtered off, air-dried, and dissolved in water for use. Reducing sugars are estimated by Bertrand's method (a) before inversion, (b) after the action of saccharase and (c) after hydrolysis (Clerget). Aldoses are estimated iodimetrically before and after complete hydrolysis of sugars (Auerbach and Bödlander). From the results, the quantities of sucrose, melitizose, maltose, glucose and fructose present are calculated.

D. G. FORBES

1344. The determination of dichloroethane and chloropicrin in aerated grain and grain products. G. A. Zakharenko and G. A. Vodaturskii. *Trudy Odessk. Tekhnol. Inst.*, 1955, (5), 46-57; *Ref. Zhur. Khim.*, 1956, Abstr. No. 26,050.—Dichloroethane (**I**) is determined by catalytic decomposition at 600° on a mixture of pure Fe_2O_3 and asbestos, prepared by igniting 2 pt. of pure ferrous oxalate with 1 pt. of short-fibred asbestos in a porcelain crucible. **I** is led to the oven by blowing air over the grain for 2 to 2.5 hr. The Cl- formed are titrated by the Volhard method. **I** is completely removed even from aerated grain that has been in

I vapour for ten days. The accuracy of the determination is within $\pm 5\%$. The method may be used for determining 0.01 g of **I**. Chloropicrin (**II**) is determined by thermal decomposition of the vapour by drawing it in a stream of H over finely divided Ni, prepared by reduction of NiO at 400° to 450° for 1 to 1.5 hr. In the decomposition of **II**, NH_3 is formed, which is absorbed in acid, the excess of acid then being titrated. By this method 0.02 g of **II** can be determined, within the limits of weighing error. **II** is not completely removed from grain by heating on a water bath and ventilating for 3 to 4 hr.; the longer the grain is subjected to the action of **II**, the more **II** will it retain (after 112 hr. action, the grain retains 29.62%; after 0.5 hr., 8.56%). Increasing the temp. of the samples tested to between 120° and 130° did not lead to complete removal of **II**.

C. D. KOPKIN

1345. Determination of the zinc content of Camembert cheese. W. Schwabe. *Dtsch. LebensmittelRdsch.*, 1955, **51** (10), 245-249.—Zinc can be detected in the rind and body of Camembert cheese prepared in dairies in zinc vessels. As the result of numerous determinations it is concluded that as a safety precaution the zinc content of cheese should not exceed 10 mg per 100 g of rind. Data from various factories are recorded showing mean values of from 30 to 40 mg of Zn per 100 g of Camembert cheese as compared with only traces or, at most, from 0.5 to 2.0 mg per 100 g of cheese, with one exception of 11.9 mg of Zn, from factories that use aluminium utensils. For the determination of Zn, the entire rind of a cheese is cut up and thoroughly mixed in a mortar; 10 g of this mixture is dried overnight in an oven at 105°; then heating is gradually increased until no more fumes are given off. The black residue is moistened with a few drops of water and crushed with a glass rod and, after evaporation at 105°, is heated in a muffle-furnace for 1 hr. at 500° to 600°; 10 ml of H_3PO_4 (25%) and 5 ml of water are added and the whole is heated over a water bath. Traces of carbon are filtered off and the filtrate (60 to 70 ml) is treated with 1 ml of 3% H_2O_2 and 25 ml of KSCN reagent (19.5 g of KSCN and 12.5 g of HgCl_2 in 500 ml of water), with stirring. After 2 hr. the soln. is filtered through a G4 sintered-glass crucible, the ppt. is washed three times with reagent and once with methanol and finally dried at 105° for 1 hr.

P. HAAS

1346. Detection of refining of lard. I. The aniline point. H. P. Kaufmann and J. G. Thieme (Dtsch. Inst. für Fettforschung, Münster, Westphalia, Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (8), 585-592.—An attempt is made to use the aniline point for the detection of refined fat in lard, and the various factors that affect this characteristic are examined. The aniline point cannot be made the basis of a specific test for refined lard, but it can sometimes be used to indicate a rancid or oxidised lard that has been subjected to treatment with bleaching-earth. The bleaching-earth removes peroxides, but compounds containing hydroxyl groups remain, and these have a marked effect on the aniline point.

E. HAYES

1347. Turbidimetric determination of gelatin. T. I. Přistoupil, V. Tomanová and J. Nikl (Inst. Haematology and Transfusion, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (3), 386-387.—The Rogers method (*Amer. J. Clin. Path.*, 1953, **23**, 638), used earlier for the determination of oxypoly-gelatin, and as a precipitation reaction with tannin,

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[Abstr. 1348-1355]

has been found suitable for the determination of gelatin in plasma, the turbidity being measured with a blue-green filter. Trichloroacetic acid must be used for removing plasma proteins.

J. ZÝKA

1348. The differentiation of colouring matter in red wines. P. Ribereau-Gayon (Lab. d'Œnologie et Chim. Agric., Bordeaux). *Ann. Falsif.*, 1956, **49**, 381-387.—A review of the methods for the differentiation of colouring matters in red wine is given and the separation of the constituents, in particular of mono- and di-glucosides, is described. The most satisfactory method is by paper chromatography and the use of differences in the solubilities of these compounds. Except in particular cases, preliminary purification is unnecessary. The fermentation process is found to have little effect on the composition of the colouring matter, but maturing of > 3 years causes various changes. The procedure is applied to distinguish wines from hybrid vines.

D. G. FORBES

1349. A rapid dielectric method for determining the oil content of safflower and sunflower seed. R. M. Johnson, W. H. Hunt, M. H. Neustadt and L. Zeleny (Grain Div., U.S. Dept. of Agric., Washington, D.C.). *J. Amer. Oil Chem. Soc.*, 1956, **33** (7), 314-316.—The rapid dielectric method for determining the oil content in oleaginous seeds (*cf.* Hunt *et al.*, *Ibid.*, 1952, **29**, 258; 1953, **30**, 463) is modified (grinding and extracting 80 g of the sample with 120 ml of *o*-dichlorobenzene) for use with sunflower and safflower seeds, with errors of 0.34% and 0.27%, respectively.

I. JONES

1350. Improved method for determining gossypol in crude cotton-seed oils. W. A. Pons, jun., D. Mitcham, R. T. O'Connor and M. F. Stansbury (S. Reg. Res. Lab., New Orleans, La., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1956, **33** (7), 324-330.—The *p*-anisidine method for the determination of gossypol in crude cotton-seed oils is modified to make it applicable to all crude oils obtained by the newer methods of processing cotton-seed. The modifications include (*i*) a change in the composition of the solvent, (*ii*), a higher reaction temperature, and (*iii*) use of a more concentrated *p*-anisidine reagent. The modified method is found to be satisfactory when different types of colorimeter and spectrophotometer are used for measuring the colour developed. Comparison of aniline and *p*-anisidine as reagents for the analysis of gossypol pigments shows that the presence of modified gossypol in some crude oils results in an over-correction for background absorption and leads to significant errors when aniline is used as the colour-development agent.

I. JONES

1351. Application of nitrometry. XIII. Determination of riboflavin. Masaharu Yamagishi, Makoto Yokoo and Saburō Inoue. *J. Pharm. Soc. Japan*, 1956, **75** (11), 1386-1389.—The decomposition of riboflavin (**I**) in NaOH soln. to urea (Kuhn *et al.*, *Ber.*, 1933, **66**, 1577), followed by nitrometry with NaOBr, was applied to the determination of **I**. Its photochemical decomposition products such as lumiflavin undergo a similar reaction, but are removed by extraction with CHCl₃. The sample (30 to 100 mg) or its phosphoric acid ester (50 to 150 mg) is dissolved in 1% acetic acid and made up to 100 ml; a 5-ml portion is shaken with CHCl₃ (5 ml) and 1 ml of the aq. layer is heated on

a water bath with *N* NaOH (1 ml). The product is cooled and submitted to nitrometry with NaOBr.

K. SAITO

See also Abstracts 1285, 1309, 1341.

Sanitation

1352. Application of X-ray emission spectrography to air-borne dusts in industrial hygiene studies. R. C. Hirt, W. R. Doughman and J. B. Gisclard (American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1649-1651.—The atmosphere is sampled by drawing the air at a known rate through a commercial air-sampler fitted with a glass-fibre filter disc. The air-borne dust, including any heavy metals, is retained in the disc, which is spray-sealed for safe transfer to the Norelco X-ray emission spectrograph. The 2.4-cm filter disc has an effective area matching that of the primary X-ray beam. Linear calibration curves extending from 5 to 100 µg have been prepared for Co, Cr, Fe, Pb, Hg, Ni, Pt, V and Zn. The limits of detectability of these elements are listed and vary from 0.5 µg of Fe to 7.8 µg of Hg.

E. G. CUMMINS

1353. Polarographic determination on solid electrodes of heavy metals in the air of industrial undertakings. I. I. B. Kogan (Ukr. Central Inst. of Occupational Hygiene and Diseases, Kharkov). *Zhur. Anal. Khim.*, 1956, **11** (3), 313-318.—Small amounts of Cu, Zn, Cd, Mn and chromates in air are collected and determined polarographically with amalgamated-silver rotating electrodes.

G. S. SMITH

1354. The determination of epichlorohydrin [1-chloro-2:3-epoxypropane] in air. J. W. Daniel and J. C. Gage (I.C.I. Ltd., Ind. Hyg. Res. Lab., The Frythe, Welwyn, England). *Analyst*, 1956, **81**, 594-598.—In the method described, a 2-litre sample of the air to be tested is drawn through 8 ml of water at ≥ 0.5 litre per min. The air-entry tube of the bubbler is removed and washed with 2 ml of water. The liquid is then treated with 1 ml of HIO₄ (0.1 M), and the loosely stoppered vessel is heated in a boiling-water bath for 20 min. The 1-chloro-2:3-epoxypropane (**I**) is thus oxidised to formaldehyde. Sodium arsenite (0.5 M) (2 ml) is added, followed by 2 ml of acetylacetone reagent (25 g of ammonium acetate, 3 ml of glacial acetic acid and 0.2 ml of acetylacetone in 100 ml of water). The vol. is adjusted to 15 ml and the yellow colour is measured either by visual comparison with dilutions of a standard K₂Cr₂O₇ soln. (0.1%, w/v) or absorptiometrically at 412 m μ . The calibration graph for the latter procedure is prepared with a standard soln. of **I**. The vapour of **I** is toxic and it is suggested that the concn. in atmospheres to which there is prolonged exposure should not exceed 20 mg per cu. m.

A. O. JONES

1355. Methods of sampling water used in industry. British Standards Inst. (2, Park St., London), B.S. 1328: 1956, 35 pp.—Methods of sampling for the chemical and physical testing of water used in industry are described, but not the sampling of water required for bacteriological testing nor the sampling of effluents. Methods are given for sampling of raw water, treated or softened water, feed water, boiler water, condensates and distillates, water from vessels under reduced pressure, water (including

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addition of reagents) for the determination of dissolved oxygen, water for special purposes, and water for continuously recording instruments. The determination of dissolved oxygen by the starch method is also described.

O. M. WHITTON

1356. Polarographic investigation of potable water and of water for industrial use. The determination of hardness and of alkalinity. J. Proszt and K. Györbiró (Inorg. Chem. Inst., Tech. Univ., Budapest). *Anal. Chim. Acta*, 1956, **15** (6), 585-591.—Milligram amounts ($\equiv 10^{-3}$ to $10^{-4} M$) of Ca^{2+} , Mg^{2+} and $(\text{Na}^+ + \text{K}^+)$ in the water can be determined rapidly by a polarographic procedure, with a modified streaming-mercury electrode. The supporting electrolyte is a 0.4 to 0.8 M soln. of tetramethylammonium chloride, the cell resistance is 340 ohms and the c.d. $\approx 10^{-4}$ amp. In contrast with the dropping-mercury electrode, the arrangement described ensures a favourable shift of E_1 , so that a sharp separation of the four waves (those of Na^+ and K^+ are very close together) is obtained and the wave heights are proportional to concn. The hardness of the water can also be determined. The max. error is $\approx \pm 4\%$ for Mg^{2+} or Ca^{2+} and $\pm 2\%$ for $(\text{Na}^+ + \text{K}^+)$.

W. J. BAKER

1357. Fluoride distillation method using controlled air jet. R. L. Morris and J. Cerny (State Hygienic Lab., Iowa City, U.S.A.). *J. Amer. Wat. Wks Ass.*, 1956, **48** (4), 449-454.—Thrun's air-flow method for determining trace fluorides in water has been made reliable and precise by exact control of the air flow and distillation rates. The apparatus comprises a 1-litre flask, acting as an air scrubber, linked to an air-flow meter which is connected to a specially constructed side jet fitted into a 300-ml long-necked Kjeldahl flask; the size of jet and its positioning are described. The Kjeldahl distillation flask is fitted with a bulb trap from which a connection leads via a condenser to a 100-ml graduated cylinder. The test water (100 ml), 10 ml of distilled water, 0.2 to 0.3 g of silver sulphate and glass beads are placed in the distillation flask, and 40 ml of conc. H_2SO_4 is carefully added without mixing. The distillation train is connected up, air flow at a constant rate is started and, after 0.5 min., heat is applied to obtain a distillation rate of 10 ml per min. When 90 ml of distillate has been collected, 10 ml of distilled water is added, and 10 ml of the mixture is removed and titrated with 0.02 N NaOH. If less than 1 ml of alkali is used, the acidity is less than 100 p.p.m. and distillation is acceptable. The remaining 90 ml is then analysed for F⁻ by any suitable colorimetric method. Data illustrating the accuracy attainable are given.

G. HELMS

1358. Photometric determination of chlorides in water. D. M. Zall, D. Fisher and M. Q. Garner (U.S. Naval Engng Exp. Sta., Annapolis, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1665-1668.—The sample is treated with excess of $\text{Hg}(\text{SCN})_2$, and the SCN⁻ liberated are allowed to react with Fe³⁺ (as perchlorate). The colour intensity is measured at 460 m μ or by visual inspection, and compared with standards. There is interference from Br⁻ and high concn. of F⁻, NO₃⁻, NO₂⁻, SO₄²⁻, PO₄³⁻, lower alcohols, tartaric acid and acetone. A sensitivity of 0.05 p.p.m. is given.

D. A. PANTONY

1359. A sensitive and rapid method for the determination of iron in natural waters. G. Almássy and M. Z. Kávai (Inst. Med. Chem., Med. Univ.,

Debrecen, Hungary). *Magyar Kém. Foly.*, 1956, **62** (9), 325-326.—To oxidise Fe²⁺ to Fe³⁺, add N HNO₃ (0.5 ml) to natural water (10 ml) and keep at 100° for 5 to 10 min. Add aniline reagent (0.5 ml) (*cf.* *Anal. Abstr.*, 1956, **3**, 414) and bromophenol blue indicator (1 drop), followed by 15% Na acetate, to bring the pH to ≈ 4.7 . Add dipyridyl reagent (0.2 ml) (*loc. cit.*) and keep the soln. in a hot-water bath for 5 min. Determine the extinction in a Pulfrich photometer, with an S50 filter and a 5-cm cell, against a blank of distilled water. The evaluation is carried out by means of a calibration curve; a blank for the reagents must also be determined. If the original water contains a ppt., shake it thoroughly before taking out a sample (50 ml), add 20% HCl (0.5 ml) and filter. Use 10.1 ml of soln. (corresponding to an original 10 ml) as described above. The sensitivity is 30 μg per litre.

A. G. PETO

1360. Emission spectra in water analysis. W. Christ. *Chem. Tech., Berlin*, 1956, **8** (5), 280-285.—A discussion is given of the methods and apparatus used for the estimation of metals in the analysis of waters by flame spectrometry and by d.c. arc spectrography. In general, the flame methods are accurate to within $\pm 10\%$ and the arc methods to within $\pm 20\%$. The use of flame photometry for determining Ca in phosphate-containing waste waters from sugar manufacture is described. In one (differential) method, photometric measurements are made of the original sample and of the sample with known amounts of CaO added, and in another method the phosphates (together with other impurities) are removed from the solution by pptn. with Fe³⁺ before photometry. Results are compared. The determination of (trace amounts of) Rb, Cs and alkaline-earth metals in natural waters is also described. The water is first boiled with saturated Ba(OH)₂ solution to precipitate Ca, Mg, Al, Fe, silica, phosphate and sulphate. The filtrate is evaporated to dryness, taken up with 1 to 3 ml of water, and again heated to dryness. Part of the dry product is arced for estimation of Li, and the rest is taken up with water, treated with sodium cobaltinitrite to precipitate the cobaltinitrite of K-Rb-Na, and this is decom. at 250° to 300°. The product is leached (from Co, etc.) with water, and treated with HCl. After addition of BaCl₂ (to show the homologous line), the resulting RbCl is submitted to spectrometry. If Cs is also present in the water it remains with the Rb throughout, and is similarly determined.

H. L. WHITEHEAD

1361. Simple method for estimating total phosphate in sewage. J. H. Howard (Cranston Print Wks. Co., Cranston, R.I., U.S.A.). *Sewage Ind. Wastes*, 1956, **28** (6), 785-786.—The Deniges colorimetric procedure, as improved by Truog and Meyer (*Ind. Eng. Chem.*, 1929, **1**, 136), is further modified so as to obviate the need for any acid other than H₂SO₄ during digestion. The method is rapid and photometry is unnecessary as visual comparison with standards suffices.

S.C.I. ABSTR.

1362. Estimation of n-butanol and ethyl Cellosolve [2-ethoxyethanol] in waste streams with Sudan III reagent. D. H. Feldman and J. C. Cavagnol (Lederle Lab. Div., American Cyanamid Co., Pearl River, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1746-1748.—The method depends on the ability of 2-ethoxyethanol to extract the violet base form of Sudan III, whereas n-butanol extracts only the red

4.—BIOCHEMISTRY

[Abstr. 1363-1370]

form. The solvent concn. in an aq. mixture need be only 1% or less. The Sudan III reagent is prepared by shaking 0.02 g of the dye with 200 g of NaCl and 500 g of K_2CO_3 . The sample waste (10 ml) is distilled with 10 ml of $N H_2SO_4$ and the first 10 ml of distillate is filtered to remove interfering amines and entrained solids; 2 ml of the filtrate is pipetted over 7 g of the reagent and the nature and extent of the extraction are observed. With neither of the two substances present there is no extraction or colour change. With a trace to 0.2%, *n*-butanol extracts a little dye as a red colour which disappears on mixing and the 2-ethoxyethanol causes the mixture to turn violet without extraction. With 0.2 to 0.5%, red or violet globules are extracted, respectively; and with 0.5 to 1.0%, large red or violet droplets. The interference of other solvents is investigated.

E. J. H. BIRCH

1363. The polarographic determination of copper in industrial effluent waters. M. S. Chizhevskaya. *Sb. Nauch. Rabot, Molotov Med. Inst., Molotov*, 1955, 79-82; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,306.—In this determination, 3 N NaCl soln. is used as the indifferent electrolyte. The height of the wave is proportional to the concn. of Cu. The method allows 5 μ g of Cu to be determined in 1 ml of soln. The polarography can be carried out in the presence of all the impurities present in the effluent water, except for organic substances, which are removed by ignition. After the determination of Cu, Zn may be determined in the same soln.

C. D. KOPKIN

See also Abstracts 1151, 1403.

Agriculture and Plant Biochemistry

1364. A spectrographic method for the determination of boron in plant ash. L. I. Obolenskaya. Report of Symposium: "Issled. Priklad. Khim. M.-L., Izd. Akad. Nauk, SSSR," 1955, 337-340; *Ref. Zhur., Khim.*, 1956, Abstr. No. 29,345.—The spectra are excited in a d.c. arc between copper electrodes. The samples of ash and standards (40 mg of each) are introduced into the discharge on paper strips steeped in $(NH_4)_2SO_4$ soln. The exposure time is 3 min. The standards are prepared by mixing salts. Boron is introduced as a soln. of borax. As internal standard, Sn as SnO_2 is added to the samples. The lines used are—B 2497.7 and Sn 2495.7 Å. A calibration curve is constructed for concn. of B from 0.001 to 0.1%. The probable error of the analytical results is $\pm 5.8\%$.

C. D. KOPKIN

1365. Vitamins in germination. Determination of free and combined inositol in germinating oats. A. Darbre and F. W. Norris (Dept. of Applied Biochem., Univ. Birmingham, England). *Biochem. J.*, 1956, 64 (3), 441-446.—Inositol in germinating oats is determined by means of *Schizosaccharomyces pombe* using a modification of a method described earlier (*Analyst*, 1956, 81, 394) whereby asparagine is eliminated from the medium and the concentration of biotin is increased 100%. Methods for the assay of total and free inositol are described. Inositol is liberated from bound forms, mainly phytin, by autolytic enzymes and by added phytase; but the best method is to heat in a sealed tube with $N HCl$ at 123° for 48 hr. Hydrolysis by phytase is almost as good, but the time of incubation is very long. Lipid inositol is separated and

assayed with difficulty, but only small amounts are present in oats.

J. N. ASHLEY

1366. Estimation of α -keto acids in plant tissue: a critical study of various methods of extraction as applied to strawberry leaves, washed potato slices and peas. F. A. Isherwood and C. A. Niavis (Low Temp. Station for Res. in Biochem. and Biophysics, Univ. of Cambridge, England). *Biochem. J.*, 1956, 64 (3), 549-558.—When hot acid or strongly alkaline media, or boiling methanol, are used to inactivate the enzymes in strawberry leaves, washed potato slices and peas, there is both formation and destruction of α -keto acids in the tissue extract during disintegration. Any method of heat inactivation, however short, may cause a significant change in the content of α -keto acid. The best method involves freezing the tissue in methanol - solid CO_2 and then disintegrating it in 0.6 M HPO_3 at -2°.

J. N. ASHLEY

1367. The determination of sulphates in aqueous extracts of soils by cation exchange. V. P. Khramov and V. S. Kolosova. *Uch. Zap. Saratov. Univ.*, 1955, 42, 93-95; *Ref. Zhur., Khim.*, 1956, Abstr. No. 36,183.—The method is based on adsorption by a cationite (H form) of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} and other cations, the release of equivalent quantities of H^+ , and acidimetric titration of the resulting soln. The content of Cl^- must be known. Any type of cationite may be used. As compared with the gravimetric method, the abs. error is 0.02 to 0.03%.

C. D. KOPKIN

1368. The microbiological assay of penicillin in feeding-stuffs. J. S. Simpson and K. A. Lees (Glaxo Lab. Ltd., Greenford, Mddx., England). *Analyst*, 1956, 81, 562-565.—A microbiological plate method with *Sarcina lutea* as test organism is described for the assay of penicillin in feeding-stuffs. The samples are extracted with 25% (v/v) acetone in a phosphate buffer soln. (pH 7.5), aliquots of the extract being diluted with the solvent to contain 0.1 and 0.05 unit per ml. Standard reference soln. of sodium benzylpenicillin are prepared in the same solvent medium. The sample and reference soln. are used directly in a standard cup-plate microbiological assay with incubation at 30° for 18 to 24 hr. The limits of error ($P = 0.95$) of the method are approximately 90 to 112% with six samples and two standards at two levels each on an 8 × 8 quasi Latin-square plate (cf. Lees et al., *Anal. Abstr.*, 1955, 2, 1648, 1649).

A. O. JONES

1369. Urease activity in soyabean-meal products. A. K. Smith, P. A. Belter and R. L. Anderson (N. Utilization Res. Branch, Peoria, Ill., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1956, 33 (8), 360-363.—A method in which direct titration of ammonia is used as a measure of urease activity is modified for use in the assay of raw and of slightly denatured soyabean meal. The modifications are—(i) the use of glutathione, (ii) a pre-soaking of the sample for 30 min. at 40°, and (iii) carrying out the assay at 40°. Data on the urease activity of several varieties of soyabeans, and for immature and frost-damaged soyabean are presented.

I. JONES

1370. Determination of organic isothiocyanates in cruciferous oil-cakes. G. Jacini and M. Barro-Raffel (Staz. Sper. Ind. Olii e Grassi, Milan). *Olio Min.*, 1956, 33 (4), 97-98.—An aqueous suspension of the cake is subjected to enzymatic hydrolysis with an extract of white mustard seed at 40° for 3

hr. It was found that higher yields of isothiocyanates were obtained at the natural pH of 5.2 to 5.4 than if the pH were changed to 3 or 7. The isothiocyanate formed is then distilled in the presence of a little alcohol and the distillate collected in aq. NH₃. The isothiocyanate is estimated volumetrically by treatment with AgNO₃ and back-titration.

L. A. O'NEILL

1371. The problem of the determination of phosphoric acid in fertilisers. G. Sánchez Marco (La Industria Química de Zaragoza, S.A., Spain). *Inf. Quím. Anal.*, 1956, **10** (5), 168-176.—The review, started previously (*cf. Anal. Abstr.*, 1957, **4**, 294), is completed. (66 references.)

D. LEIGHTON

1372. Chromatographic determination of 2-sec.-butyl-4: 6-dinitrophenol [DNBP] [dinoceb] in weed killers. W. C. E. Bouwman and L. Westenberg (Plantenziektenkundige Dienst, Wageningen, Holland). *Chem. Weekbl.*, 1956, **52** (46), 827.—The method described is more selective than those previously recommended. A suitable quantity of material is shaken in a separating funnel with water containing a little HCl and hexane to remove basic substances; the aq. layer is shaken twice more with hexane, and the combined hexane extracts are greatly diluted to contain about 2 mg of dinoceb per ml. A chromatographic column (height about 18.6 cm) is packed with cellulose powder that has been ground with a mixture of phosphate buffer and hexane. The dinoceb soln. (1 ml) is added and washed through with the buffered hexane. Of the three or four yellow zones that appear, the uppermost contains the dinoceb. The first 17 ml of eluate is discarded, and the following 13 ml, which contains all the dinoceb, is shaken three times with a total of 20 ml of 2 N NaOH diluted with 100 ml of water. The combined aq. phases are made up to 200 ml and filtered through 1 g of kieselguhr. The extinction is measured at 375 m μ and the concn. is determined from a standard curve prepared from pure dinoceb dissolved in 0.2 N NaOH.

P. HAAS

1373. A kinetic method for determining the γ -isomer of hexachlorocyclohexane in dusts and in concentrated preparations. S. M. Shogam and E. I. Fen'kova. *Sb. Rabot. Nauch. Inst. Udobr. i Insektifungisidam*, 1955, (156), 30-36; *Ref. Zhur., Khim.*, 1956, Abstr. No. 43,582.—For elimination of the non-reproducibility of results obtained in determining the γ -isomer by an earlier method (La Clair, *Anal. Chem.*, 1948, **20**, 241) it is suggested that quantities of ethanolic soln. of alkali, free from CO₂, and equivalent to 10 ml of *N* soln., are cooled in an ice bath and added to tubes containing cooled ethanolic soln. of weighed samples. Blank soln. are also prepared without the addition of alkali. After standing in the ice bath for 15 min., the alkali is added and stirred continuously for 8 to 10 min. and then periodically during 50 min. Chloride is determined by titration with AgNO₃, and the percentage of γ -isomer is found from the formula— $x = 25.3/(a - b) - 14.6$, where *a* is the vol. (ml) of 0.1 N AgNO₃ soln. used on the second sample; *b* is the same for the blank. The reproducibility of results is ± 0.05 ml of 0.1 N AgNO₃. The divergence from results obtained by the chromatographic method is < 1% for technical products, 0.5 to 2.5% for conc. products and 0.1 to 0.15% for dusts.

R. LORD

1374. Detection of Gammexane in the presence of DDT in insecticides. E. Weber (Imhausen Werke G.m.b.H., Witten, Ruhr, Germany). *Z. anal. Chem.*, 1956, **153** (4), 270-271.—More complete experimental details of the method previously described (*Ibid.*, 1951, **134**, 32) are given.

P. S. STROSS

1375. New colorimetric micro-method for determination of tetraethyl pyrophosphate. R. M. Fournier. *Chim. et Ind.*, 1956, **76** (2), 246-247.—The use of tetraethyl pyrophosphate (**I**) as an insecticide has necessitated the development of a method of micro-determination of **I** in the atmosphere. The method described is based on saponification and oxidation of **I** with aq. (NH₄)₂S₂O₈ (10%), followed by treatment with 10 N H₂SO₄, aq. (NH₄)₂MoO₄ (7.5%) and aq. SnCl₂ (0.2%); the resulting colour (after 4 min.) is measured photometrically, with a red filter, at 640 m μ .

S.C.I. ABSTR.

See also Abstracts 1344, 1376.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

1376. Modification of Christy and Norris mill to avoid iron contamination of ground plant-materials. A. W. Palm and R. S. Beckwith (C.S.I.R.O., Adelaide, Australia). *Anal. Chem.*, 1956, **28** (10), 1637-1638.—Simple modifications to a Christy and Norris mill, to make it suitable for grinding plant-material without contamination by micro amounts of nutrient metals, are described. The interior of the grinding chamber and the exit and inlet openings were coated with a suitable plastic, free from iron, and the back plate and revolving beater were electroplated with a thick layer of chromium. Poly(methyl methacrylate) sheet was used for the feed chute, and the sieve of the original mill was replaced by one fabricated in laminated plastic. Other parts were nickel-plated and then coated with glossy enamel.

G. P. COOK

1377. Drawing conventions for laboratory glass apparatus. British Standards Inst. (2 Park St., London). B.S. 2774:1956, 20 pp.—Conventions are recommended for drawings of laboratory apparatus, principally of glass, such as are required for working drawings and for drawings for inclusion in British Standards, textbooks, and technical journals and reports.

O. M. WHITTON

1378. An automatic pipette with a device for use in delivery. H. Schweizer (Landwirtschaftliche Versuchsanstalt, Zürich-Oerlikon, Switzerland). *Chimia*, 1956, **10** (8), 194-195.—The pipette described and illustrated can be adjusted to any convenient height and is supported on an arm which can move in a horizontal direction on a pivot attached to a vertical rod. The filling of the pipette is started by suction from a water pump and is interrupted by moving the arm through 45°, while a series of receptacles arranged on a revolving table can be moved into position for the next delivery. It is claimed that a considerable saving of time is effected by the use of the outfit and that the life of the pipettes is much greater than that of the usual type.

P. HAAS

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

[Abstr. 1379–1386]

1379. Apparatus for the determination of distillation range. British Standards Inst. (2 Park St., London). B.S. 658:1952. Amendment No. 1 (published 27 September 1956).—Amendments are published in the diameter of the hole in the hard asbestos shelf and in the correction of barometric pressure to 0° .
N. E.

1380. A new apparatus for analyses involving distillation. Application to the estimation of fluorine. Y. Berquin (Lab. de Contrôle des Fabrications de l'Usine de Villeneuve-la-Garenne, France). *Chim. Anal.*, 1956, **38** (10), 367–368.—A modified distillation apparatus for the estimation of F is described. The lead from a steam generator is joined below the stopper of a tap-funnel welded into a 500-ml distillation flask. A closed tube sealed inside the bulb of the flask, and reaching to the bottom, carries a thermometer. The vapours from the boiling sample are carried by a wide, vertical, vacuum-jacketed tube (to condense extraneous vapours), fitted to the flask with a ground glass joint, to the top of a condenser, also arranged vertically to allow vapours to condense into a receiver placed below it. A ground glass stopper at the top of the condenser permits washing at the end of the distillation. The method used for the final estimation of F is that of Willard and Winter (*Anal. Chem.*, 1933, **5**, 7). *Procedure*—Weigh into the flask ≥ 25 g of the sample containing between 10 and 100 mg of F, quartz (0·5 g) and water (150 ml). Set up the apparatus with the condenser adapter dipping into some water in a calibrated 500-ml flask receiver. Introduce HClO_4 (65%) (50 ml) through the tap-funnel and, with very little steam passing, heat the mixture to 120° . Turn the steam on full and continue heating until a temp. of 165° is reached. Allow the apparatus to cool and wash out the condenser into the receiver. Neutralise the distillate with NaOH soln. (30%) in the presence of three drops of Na alizarinsulphonate soln. and dilute to 500 ml. If an appreciable amount of H_3PO_4 is present in the distillate, redistil. Fluorine is estimated in the distillate by the usual method with standard $\text{Th}(\text{NO}_3)_4$ soln.
D. G. FORBES

1381. Manostat and receiver for vacuum distillation on columns. M. I. Rozengart, A. L. Liberman and D. M. Dubinin (Inst. of Org. Chem., Acad. Sci., U.S.S.R.). *Zhur. Anal. Khim.*, 1956, **11** (3), 351–354.—Apparatus for vacuum fractional distillation with means for keeping the pressure constant during distillation and for collecting an unlimited number of fractions is described.
G. S. SMITH

1382. A new type of fraction collector. U. Hollstein and B. Cazemier (Lab. v. Org. Scheikunde, Univ. Amsterdam, Holland). *Chem. Weekbl.*, 1956, **52** (48), 853.—A description is given of an apparatus which automatically collects a constant vol. of eluate flowing from a column engaged in chromatographic separations. The fractions are run into siphons of various sizes to hold from 1 to 10 ml of liquid. A given siphon is suspended from one arm of a balance and is counterpoised on the other arm by a wt. such that at a moment before the required vol. of liquid siphons over and makes the arm drop, a switch is pressed, causing a magnetic escapement to allow a disc holding the collecting tube to revolve and replace the filled tube by an empty one; the device allows the collecting tube to remain long enough under the siphon to catch any drip. The apparatus (illustrated) is simple to construct and easy to handle.
P. HAAS

1383. Multiple development in strip and circular chromatography. H. C. Chakrabortty and D. P. Burma (Bose Research Inst., Calcutta, India). *Anal. Chim. Acta*, 1956, **15** (5), 451–456.—In the multiple-development technique of paper chromatography, theoretical consideration shows that the separation between two spots should increase if the sum of their R_F values is < 1 , the separation should decrease if this sum is > 1 , and there should be no change if the sum = 1. Experiments with amino acids support these findings and, although changes in R_F values in successive developments cause deviations, the rule is of useful application in the design of experiments in strip and circular paper chromatography.
W. C. JOHNSON

1384. An apparatus for eluting and concentrating chromatogram spots. F. G. Tryhorn and A. S. Curry (Home Office Forensic Science Lab., 32 Rutland Drive, Harrogate, England). *Nature*, 1956, **178**, 1180.—The apparatus, which is easily made from a length of 1-mm-bore capillary tubing, is designed to elute and concentrate small quantities of alkaloids from paper chromatograms, but would also be applicable to other problems requiring continuous extraction and concentration of micro quantities. With this apparatus, 50 μg of strychnine from a chromatogram run in butanol-acetic acid was quantitatively recovered and concentrated into 0·1 ml of ethanol. The apparatus, coupled with paper chromatography and the use of micro-cells for u.v. spectrophotometry, enables accurate determinations to be made of small quantities (e.g., 100 μg) of alkaloids such as atropine, which have very low specific extinction coefficients.
K. A. PROCTOR

1385. Use of anionite paper for quantitative analysis of some anions. A. Lewandowski and J. Ignasiak (Dept. of Gen. Chem., Poznan Univ., Poland). *Roczn. Chem.*, 1956, **30** (2), 559–567.—Anionite paper, prepared by Witkowsky's method (cf. *Anal. Abstr.*, 1957, **4**, 1386), is converted into the OH form, and strips are used for ascending chromatography of acids. The strips are developed by spraying with indicator solution, and the area of the spot is proportional to the concn. of acid. Salts are determined similarly, after first passing the solutions through a strip of cationite paper (H form). Since the area of the spot varies for equal concn. of different acids, solutions containing various anions (Cl^- , SO_4^{2-} , NO_3^-) are first passed through a strip of paper impregnated with $\text{Ba}(\text{NO}_3)_2$ and TiNO_3 , inserted between the cationite and anionite strips, to remove Cl^- and SO_4^{2-} , when the spot representing total anion concn. will be due to HNO_3 alone. Further refinements of the method consist in allowing the solution to pass successively through cationite paper ($\text{Ba} + \text{Ag}$ form), cationite paper (H form), $\text{TiNO}_3 + \text{Ba}(\text{NO}_3)_2$ paper, and anionite paper (OH form). The error for 0·01 to 0·06 N single acids and salts is about $\pm 3\%$, but much greater errors are obtained for mixtures.
R. TRUSCOE

1386. Cationite paper. H. Witkowsky (Dept. of Gen. Chem., Poznan Univ., Poland). *Roczn. Chem.*, 1956, **30** (2), 549–557.—Cellulose pulp is mixed with exchange resins (0·2 g per g of cellulose), and the mixture is formed into paper, strips of which are washed with acid and water, and used for ascending chromatography of solutions containing $< 0\cdot1$ mg of the cation to be determined. After all the solution has entered the paper, the process is continued with a small amount of water, and the paper

is developed with appropriate reagents, when the area of the spot is proportional to the amount of cation.

R. TRUSCOE

1387. A new detector for vapour-phase chromatography. J. Harley and V. Pretorius (Dept. of Phys. Chem., Univ. Pretoria, S. Africa). *Nature*, 1956, **178**, 1244.—The detector, which can detect 10^{-12} mole of a substance, is easily constructed and is of wide applicability. It consists of a small platinum-disc cathode and a tungsten-wire anode forming one arm of a Wheatstone bridge, which is supplied with 900 V from a stabilised d.c. source. The bridge is balanced with carrier gas flowing through the detector at a pressure sufficiently low to produce a normal glow discharge between the electrodes. Compounds eluted from the column then cause a voltage change across the detector, which can be measured by a recording potentiometer.

K. A. PROCTOR

1388. Cone-plate viscometer. Comparison with coaxial cylinder viscometer. R. McKennell (Ferranti Ltd., Manchester, England). *Anal. Chem.*, 1956, **28** (11), 1710-1714.—The flow curves of materials with either Newtonian or anomalous flow properties, from paints and inks to concentrated polymer solutions, i.e., shear rates ranging from 20,000 sec. $^{-1}$ to 0.01 sec. $^{-1}$, respectively, may be plotted in < 1 min. by using an automatic recorder with the viscometer described. Filling, cleaning and temperature stabilising can be completed in 30 sec.

E. G. CUMMINS

1389. Instruments for the physical testing of paints. M. Voituriez. *Peint.-Pigm.-Vern.*, 1955, **31** (11), 971-974.—A review is presented which covers instruments for testing liquid paints (viscometers, fineness-of-grind gauges, etc.) and paint films (instruments for the measurement of opacity, thickness, hardness, impact resistance and other mechanical properties).

D. R. DUNCAN

See also Abstract 1313.

Optical

1390. Use of counter tubes in X-ray analysis. W. Parrish and T. R. Kohler (Philips Lab., Irvington-on-Hudson, New York, U.S.A.). *Rev. Sci. Instrum.*, 1956, **27** (10), 795-808.—The performance and properties of end-window Geiger counters, side-window proportional counters and NaI(Tl) scintillation counters for X-ray (5 to 50 kV) analysis are reviewed. Proportional and scintillation counters have resolving times of the order of 0.25 μ sec., giving pulse amplitudes proportional to the energy of the X-ray quanta. G. SKIRROW

1391. Two years' industrial experience with the flame photometer, colorimeter and spectrometer. H. Zoellner. *Ber. dtsch. keram. Ges.*, 1956, **33** (2), 39-46.—Various types of German, Dutch and American apparatus are reviewed and general advice is given on the choice of apparatus for flame photometry, colorimetry, nephelometry and the measurement of reflectance and transparency. The following parts of the flame photometer are discussed in some detail—(i) the flame and choice of gas (air - C_2H_2 is recommended for the analysis of glasses because it excites the alkalis more selectively), (ii) the gas-pressure regulator and gauge, (iii) the spray, (iv) the light source and the optical system, and the photometer. Details are given of

the methods adopted by Didier-Werke A.-G. for the determination of alkalis, CaO , Al_2O_3 , Fe_2O_3 , TiO_2 and SiO_2 . For the flame-photometric determination of alkalis and CaO , the sample is dissolved in HF - $HClO_4$ (HF - HCl is not active enough and HF - H_2SO_4 has a great tendency to spurt, especially if much org. matter is present) and the sesquioxides are separated with aq. NH_3 . For the colorimetric determination of Fe_2O_3 , Al_2O_3 and TiO_2 , the sample is dissolved with HF - H_2SO_4 or fused with Na_2CO_3 or with Na_2O_2 in a nickel crucible; TiO_2 is determined by the peroxide colour (450 m μ ; at 420 m μ there is considerable interference by Fe_2O_3), and Fe_2O_3 with KSCN (550 m μ), Al_2O_3 with Eriochrome cyanine (600 m μ) and SiO_2 with $(NH_4)_2MoO_4$ (435 m μ).

J. A. SUGDEN

1392. Cyanogen - oxygen flame. New source for quantitative determination of microgram amounts of metals. B. L. Valley and A. F. Bartholomay (Harvard Med. Sch., Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1753-1755.—The use of the cyanogen - oxygen flame as a spectrochemical source for the quantitative determination of Al, Ba, Ca, Co, Cr, Cu, Fe, Pb, Mg, Mn, Ni and Sr is described and some working curves are presented. Absolute amounts ranging from 0.36 to 36.0 μ g of metals may be determined.

E. G. CUMMINS

1393. Some effects of an air blast on spark discharges. B. Cragg and J. K. Hurwitz (Dept. of Mines, Ottawa, Ontario, Canada). *J. Opt. Soc. Amer.*, 1956, **46** (10), 889-895.—From the experiments described it is concluded that the "quenching" of the arc-like portion of an over-damped discharge by an air-blast produces a spectrum very similar to that excited by an oscillatory discharge. Consequently the use of an air blast defeats the purpose of using an arc-like discharge for its high sensitivity, since the discharge is converted into one that is spark-like. However, the air blast does increase reproducibility slightly and eliminates differences in analytical results due to heat treatment and sample size.

B. S. COOPER

1394. Quantitative spectrography of powdered samples on dish-shaped copper electrodes. J. P. Dvořák and J. Mandelik (Ústí nad Labem, Czechoslovakia). *Chem. Listy*, 1956, **50** (5), 738-742.—A method for the spectrographic determination of Si in raw materials and products containing fluorine was developed. Various factors having an influence on the values of $\log I/I_0$ were studied. The same procedure can be used for the determination of Li in lepidolites. The approximate error is $\pm 5\%$.

J. ZÝKA

1395. Modification of a Beckman model DU quartz spectrophotometer for measurements to 192 m μ . L. W. Taylor and L. C. Jones, jun. (Shell Oil Co., Wood River, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1706-1709.—This modification involves rotation of the collimating mirror, construction of a new wavelength scale, substitution of a photomultiplier with a fused silica window for the usual detector, replacement of the Beckman ultraviolet source with an Allen - Nester hydrogen discharge tube, use of thin-spacer absorption cells, and installation of a Vycor filter for measurement of the residual stray energy.

E. G. CUMMINS

1396. Multiple thickness cell assemblies. Application to ultra-violet spectrophotometry. D. D. Tunnicliff (Shell Development Co., Emeryville, Calif.,

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

[Abstr. 1397-1406]

U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1657-1660.—Details of the design and use of multiple-cell assemblies for the Cary and Beckman DU spectrophotometers are discussed. These cells, of different thicknesses, are joined in series, and filled in turn. A three-cell assembly for gases, and five-cell assemblies for liquids, requiring 25 ml of solution, are described.

E. G. CUMMINS

1397. Gelatin capsules for potassium bromide infra-red technique. B. M. Mitzner (Army Chemical Center, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1801.—The storing of aliquots of ground KBr of low water content and known weight is discussed (*cf. Anal. Abstr.*, 1956, **3**, 3510). E. G. CUMMINS

1398. Refractive index of liquids at elevated temperatures [instruments for measurement of]. J. L. Lauer and R. W. King (Sun Oil Co., Norwood, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1697-1701.—Two instruments for the measurement of refractive index are described. One makes use of minimum deviation principles for temperatures between 25° and 55°; the other, for temperatures from 60° to 100°, is based on the design of Eykman. Refractive indices, with respect to air at 80° and 100° and six wavelengths, for three calibration standard hydrocarbons and six other hydrocarbons are tabulated. Data concerning the relationship between refractive index and density are listed and used to check the Eykman function $C = (n^2 - 1)/d(n + 0.4)$, where C is a constant independent of temp. and pressure.

E. G. CUMMINS

1399. Analysis of D₂O/H₂O by the interferometer. Susumu Namba (Sci. Res. Inst. Ltd., Komagome, Tokyo). *Rev. Sci. Instrum.*, 1956, **27** (10), 872-873.—The use of the Riken interferometer is described. Over the range 0 to 6% of D₂O, a sensitivity of 0.05 mole-% is obtained; with suitable temp. control, a sensitivity of 0 to 0.001 mole-% is possible.

G. SKIRROW

1400. Potting of photomultipliers for use with liquid scintillation detectors. G. E. Thomas, jun. (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Rev. Sci. Instrum.*, 1956, **27** (10), 878.—A method is described for constructing robust mobile liquid scintillation detectors in which the photomultipliers are in direct contact with the liquid. The unit is readily removable, is inert to organic soln., and does not contaminate the scintillator.

G. SKIRROW

Thermal

1401. A thermistor temperature recorder. B. M. Zeffert and R. R. Witherspoon (Army Chemical Center, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1701-1705.—Automatic linear recording of temperatures in the range -80° to 32° has been achieved with the apparatus described, which employs a Leeds and Northrup Speedomax recorder, with a maximum error of 0.05°.

E. G. CUMMINS

Electrical

1402. An automatic circuit-interrupter for ensuring water circulation. P. Navellier (Lab. Municipal de Paris). *Ann. Falsif.*, 1956, **49**, 401-402.—Frustration of experiments due to the failure of the supply of cooling water in condensers employed in

conjunction with electrical heating can be avoided by use of a mercury switch controlled by the flow of water. A device is described which comprises a cylindrical, round-bottomed cell with an inlet jet sealed into the lower end and a wide overflow at the top. A T-shaped vane rests with the horizontal arm across the top of the cylinder and the vertical arm hangs in front of the inlet jet. The jet is arranged in series with the condenser of the apparatus to be controlled, and water issuing from it rocks the vane so that contact is made in the heating circuit through a mercury switch carried at one end of the horizontal arm. By adjustment of a counterpoise at the other end of the arm, the point at which the switch cuts in is made to depend on the flow of water striking the vane.

D. G. FORBES

1403. Instrument for the measurement of salinity in estuaries. E. G. Sandels (Hydraulics Res. Sta., Wallingford, Berks., England). *J. Sci. Instrum.*, 1956, **33** (1), 424-428.—A radio-frequency voltage is applied to a circuit comprising a conductivity tube and a linear variable capacitor. The voltages across each are rectified and subtracted, and for zero difference there is a relationship between capacitance and conductivity. Temperature is measured by a mercury thermometer by measuring the capacitance between the mercury column and an electrode round the stem. The salinity is computed from a nomogram. The accuracy is within $\pm \frac{1}{2}$ part per thousand over a salinity range of 0.2 to 50 parts per thousand.

G. SKIRROW

1404. Electrochromatography in the separation of ions. Anil Kumar Majumdar and Hari Gopal Mukherjee (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1956, **15** (6), 547-550.—The separation of Cu, Cd, Pb, Bi, Co and Ni from binary, ternary and quaternary mixtures thereof can be effected by electrochromatography on Whatman No. 2 filter-paper (44 cm × 1 cm) at 150 V for 5 to 10 hr. The apparatus and procedure are described, and relative migration rates and separations of the ions in various electrolytes (*e.g.*, 0.1 N HCl, NH₄Cl, Na citrate, tartaric acid) are reported. Complete separation is not possible for quinary mixtures, although the component ions can be identified.

W. J. BAKER

1405. A method of recording a.c. polarograms on a conventional d.c. polarograph. D. M. Miller (Sci. Service Lab., Canada Dept. of Agric., London, Ontario, Canada). *Canad. J. Chem.*, 1956, **34** (7), 942-947.—A method of converting a conventional d.c. recording polarograph (Sargent Model XXI) to one that will produce a.c. and d.c. polarograms is described. The conversion should be applicable to any instrument that employs a self-balancing potentiometer-type recorder utilising a 60-cycle vibrator-converter and an a.c. amplifier.

K. A. PROCTOR

1406. Analytical applications of the hanging mercury drop electrode. J. W. Ross, R. D. DeMars and I. Shain (Univ. of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1768-1771.—This electrode has been applied to the reduction of Zn²⁺, Cd²⁺, Pb²⁺ and Ti⁴⁺ in a recording instrument. Replicate runs give results with an average deviation $> 2\%$, scanning at either 0.0139 or 0.0278 V per sec. with a total recording time of < 1 min. Theoretical and experimental values of peak current are tabulated and two-component systems discussed.

E. G. CUMMINS

1407. New type of polarographic micro vessel. L. Jenšovský (Inst. Hyg. and Ind. Diseases, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (3), 398.—The vessel described is suitable for analysing 0·1 ml of the solution, and is convenient for routine determinations. Molybdenum wire is used as reference electrode.

J. ZÝKA

1408. Some applications of the differential galvanometer in polarography. E. Barendrecht (Central Lab. of the Dutch State Mines, Geleen, Netherlands). *Anal. Chim. Acta*, 1956, **15** (5), 484-491.—A description is given of some advantages of the differential galvanometer in normal, differential and derivative polarography.

W. C. JOHNSON

1409. Direct counting of tritium-tagged solid and liquid samples. F. L. Jackson and H. W. Lampe (Procter and Gamble Co., Cincinnati, Ohio U.S.A.). *Anal. Chem.*, 1956, **28** (11), 1735-1737.—The use of a windowless gas-flow counter for the direct counting of tritium-labelled solid and liquid samples is discussed. Results are reproducible with a standard deviation of 4 and 6% for infinitely thick and infinitely thin samples, respectively.

E. G. CUMMINS

1410. A windowless flow-type Geiger counter for the assay of solid materials containing soft β -emitting isotopes. T. E. Banks, L. W. Blow and G. E. Francis (Dept. of Physics and Biochem., Med. Coll. of St. Bartholomew's Hosp., London). *Biochem. J.*, 1956, **64** (3), 408-411.—The counting gas mixture is arranged to flush air from a second sample while the first sample is being counted. The counter has a low background count rate; for ^{14}C or ^{35}S it is 3 to 4 times more efficient than commercial thin-window Geiger counters, and it can be used for measuring ^3H .

J. N. ASHLEY

1411. A general method of electrochemical titration using two polarised micro-electrodes made of the same metal. I. Theory of the method. J.-E. Dubois and W. Walisch. *Compt. Rend.*, 1956, **242**, 1161-1164.—A new electro-titration method for general use is described; although simpler it is claimed to have all the advantages of the standard

amperometric method. Two micro-electrodes (E_A , E_C) of Pt are fixed in the titration cell; the applied e.m.f. is 3 V, the resistance is 0·3 meghm, and the electrolysis current is \approx 4·5 to 5 mA. After introducing a known vol. of the sample soln. into the cell, the changes in e.m.f. ($E = E_A - E_C$) between the two electrodes are measured continuously during the titration. The value of E changes rapidly at the end-point. Titration curves for 0·001 N HCl against 0·01 N $\text{Ba}(\text{OH})_2$ are reported.

W. J. BAKER

1412. Filter-paper support for mounting and assay of radioactive precipitates. B. Bloom (U.S. Dept. of Health, Education and Welfare, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (10), 1638.—The support described is designed to facilitate the transfer of a filter-paper and ppt. from suction flask to counting assembly. It has been used in the preparation of barium carbonate mounts and in the assay of Ca oxalate and uric acid.

K. A. PROCTOR

1413. R.Rf. [rectified radio-frequency] methods of chemical analysis and chromatograph zone location. A circuit combining "full-wave rectification" with "negative zero set-back." G. G. Blake (Univ. Sydney, N.S.W., Australia). *Anal. Chim. Acta*, 1956, **15** (4), 342-344 (in English).—The new circuit described and illustrated ensures increased sensitivity when using Blake's rectified radio-frequency impedance method of chromatographic zone location and of conductimetric analysis (cf. *Anal. Abstr.*, 1956, **3**, 1956, 3236; 1957, **4**, 770). The radio-frequency field at the electrodes of the zone localiser is increased and the range of the instrument is extended.

W. J. BAKER

1414. The presentation of electronic absorption spectra. G. H. Beaven and E. A. Johnson (Nat. Inst. Medical Research, Mill Hill, London). *Photo-electr. Spectr. Gr. Bull.*, 1956, (9), 211-214.—The relative merits are discussed of the different units that may be used in plotting electronic spectra, i.e., wavelength or wave number for the abscissa, and absorbance (extinction), molar extinction coefficient (ϵ) or $\log \epsilon$ for ordinate.

K. A. PROCTOR

See also Abstract 1313.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	$m\mu g$
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α
coefficient	coeff.	ounce	oz
concentrated	conc.	parts per million	p.p.m.
concentration	concen.	per cent.	%
constant	const.	per cent. (wt. in wt.)	% (w/w)
corrected	(corr.)	per cent. (wt. in vol.)	% (w/v)
crystalline	{ cryst.	per cent. (vol. in vol.)	% (v/v)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	ρ	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep.
dilute	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	n_A^F
electromotive force	e.m.f.	relative band speed	R_F
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	$E_{\frac{1}{2}}$	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	$[\alpha]_D$
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μg (not γ)	volt	V
microlitre	μl	volume	vol.
micromole	μ mole	watt	W
micron	μ	wavelength	λ
milliamperc	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	α	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II} , Mo^V . Substances in the ionic state are represented by Na^+ , Fe^{2+} , Fe^{3+} , etc., for cations and by Cl^- , SO_4^{2-} , PO_4^{3-} , etc., for anions.

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